# I. IRREVERSIBLE THERMODYNAMICS OF SYSTEMS CONTAINING RADIATION. APPLICATION TO PHOTOCHEMICAL REACTIONS

# II. MEAN VALUES IN ENSEMBLES OF SYSTEMS OF PARTICLES WITH LONG-RANGE POTENTIALS

# III. APPROXIMATIONS TO TIME-DEPENDENT ENSEMBLE AVERAGES

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# ABSTRACT

## I

The general theory of the irreversible thermodynamics of chemically reacting systems interacting with radiation is developed. From this, a limit to the efficiency of photochemical processes is derived, and this is compared with approximate experimental efficiencies of published researches, which are found to be considerably lower.

## II

A general cluster method of obtaining approximations to ensemble averages of functions depending on coordinates and/or momenta at a single time is derived, starting with a method, due to Mazo and Zemach, valid only for short-range forces, and proceeding to a method capable of treating systems of particles with long and short-range potentials, such as ionic solutions.

## III

Approaches to the time evolution of distribution functions and to time-correlation functions are discussed. A general perturbation series approach to time-correlation functions through the exponential Liouville operator is derived, and this is applied to the calculation of the first-order correction to a Fokker-Planck friction constant and to first and second-order corrections to a momentum autocorrelation function.

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# I. IRREVERSIBLE THERMODYNAMICS OF SYSTEMS CONTAINING RADIATION. APPLICATION TO PHOTOCHEMICAL REACTIONS.* (1)

## A. INTRODUCTION

The behavior of a radiation field in the presence of absorbing matter has been extensively studied, largely from the point of view of astrophysical applications. (2) The chemical study of the interaction of radiation and matter has been largely concerned with such topics as quantum yields and the mechanisms of photochemical reactions. Of particular interest are those photochemical reactions which proceed with a positive free-energy increment (i.e., which will not go "in the dark"). Typical important examples are photosynthesis and ozonization of oxygen in the upper atmosphere. In this section of the thesis we give a general treatment of the irreversible thermodynamics of systems containing radiation and apply our results to the determination of the efficiency of photochemical reactions which will not go "in the dark." Although most of the complication inherent in the general treatment will be unnecessary for the particular application which we make, we nevertheless present it here, for it is not without intrinsic interest and possible applicability.

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* This part of the thesis is a revision of a published article, reference 1.

## B. GENERAL THEORY

If unpolarized radiation is in thermal equilibrium with matter at a temperature $T$, Planck (3) has shown that the specific intensity of the radiation is given by

$$I_\nu(\underset{\sim}{n}) = \frac{2h\nu^3}{c^2}\,\frac{1}{\exp(h\nu/kT) - 1} \quad , \tag{1}$$

where $I_\nu(\underset{\sim}{n})$ is the specific intensity in units of energy per unit area per unit time per unit solid angle per unit frequency interval, and $\underset{\sim}{n}$ denotes a unit vector giving the direction. The constant $h$ is Planck's constant, $\nu$ is the frequency, $c$ is the velocity of light, $k$ is Boltzmann's constant, and $T$ is the temperature of the matter in equilibrium with the radiation. In the case of equilibrium, one can speak of $T$ as being the temperature of the radiation, $T_r$ . However, Planck (3) has also shown that it is often convenient to ascribe a temperature $T_r$ to nonequilibrium radiation, defined by equation 1, which can be solved for $T_r$ :

$$T_r = \frac{h\nu}{k\ln\left[\left(2h\nu^3/c^2 I_\nu\right) + 1\right]} \quad . \tag{2}$$

Although $T_r$ is now a function of position, direction, and frequency, it is a useful concept when the radiation can be considered to be in local thermodynamic equilibrium, which is assumed to be the case in the following development.

The system under consideration is assumed to be composed of a fluid and radiation from an outside source. Discontinuities in the fluid are supposed to be negligible. Symbols will be introduced as needed, generally following the notation of Kirkwood and Crawford (4), who give a discussion of the macroscopic equations of transport for systems not containing radiation. The Stokes' operator will be written as a total derivative, while a derivative taken at a fixed point in the coordinate system will be written as a partial derivative. Thus,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \underset{\sim}{v} \cdot \nabla \quad . \tag{3}$$

The system is described by the following equations: a) the energy-balance equation, which will be developed in detail below; b) the equation of motion of matter,

$$\rho \frac{d\underset{\sim}{v}}{dt} = \rho \underset{\sim}{X} + \nabla \cdot \underset{\approx}{\sigma} \quad , \tag{4}$$

where $\underset{\approx}{\sigma}$ is the total stress tensor, $\underset{\sim}{X}$ is the external "body" or "volume" force, $\underset{\sim}{v}$ is the macroscopic local velocity, and $\rho$ is the density of the fluid; c) the equations of continuity of the chemical species present ,

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \left( \underset{\sim}{j_i} + \rho_i \underset{\sim}{v} \right) = \rho \sum_{k=1}^{t} \nu_{ik} \frac{d\lambda_k}{dt} \quad , \tag{5}$$

where $\rho_i$ is the density of the ith component, $\underset{\sim}{j_i}$ is the diffusion flux of this component relative to the local center of mass, $\nu_{ik}$ is the stoichiometric coefficient in mass units for the ith component and the kth reaction, and $\lambda_k$ is the progress variable of the kth reaction, also in mass units; and the sum of these equations, the equation of continuity of matter,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underset{\sim}{v}) = 0 \qquad ; \qquad (6)$$

and d) the equation of transfer of radiation, of which only a consequence will be needed:

$$\rho \epsilon = - \nabla \cdot \underset{\sim}{F} - \frac{\partial \widetilde{E}_r}{\partial t} \quad , \qquad (7)$$

where $\rho\epsilon$ is the rate of energy absorption per unit volume by the matter from the radiation field, $\widetilde{E}_r$ is the space density of radiant energy, and $\underset{\sim}{F}$ is the radiant energy flux, defined by

$$\underset{\sim}{F} = \hat{e}_x \iint I_\nu \ell \, d\nu \, d\Omega + \hat{e}_y \iint I_\nu m \, d\nu \, d\Omega + \hat{e}_z \iint I_\nu n \, d\nu \, d\Omega \, , \qquad (8)$$

where the $\hat{e}$ are unit vectors in the x, y, and z directions and $\ell$, $m$, and $n$ are direction cosines taken from the same directions.

An energy-balance equation is obtained by equating the sum of the rate of increase of energy in an arbitrary region of the system,

$$\int_V \frac{\partial}{\partial t}\left(\rho E_h + \frac{1}{2}\rho v^2 + \widetilde{E}_r\right) dV \quad , \qquad (9)$$

and the rate of energy efflux through the surface of the region,

$$\int_A \left[ \underset{\sim}{j}_E + \left(\rho E_h + \frac{1}{2}\rho v^2\right)\underset{\sim}{v} + \underset{\sim}{F} \right] \cdot dA \quad , \qquad (10)$$

to the rate at which work is done on the matter in the region,

$$\int_V \sum_{i=1}^{s} \underset{\sim}{j}_i \cdot \underset{\sim}{X}_i \, dV + \int_V \rho \underset{\sim}{v} \cdot \underset{\sim}{X} \, dV + \int_A \underset{\sim}{v} \cdot \underset{\sim}{\sigma} \cdot d\underset{\sim}{A} \quad . \qquad (11)$$

Forces due to reflection of radiation at discontinuities, such as the boundary of the system, are neglected.

The surface integrals are transformed by using Gauss' divergence theorem, after which the integrands may be equated, since the region of integration is arbitrary. This gives

$$\frac{\partial}{\partial t}\left(\rho E_h + \frac{1}{2}\rho v^2 + \tilde{E}_r\right) + \nabla \cdot \left[ \underset{\sim}{j}_E + \left(\rho E_h + \frac{1}{2}\rho v^2\right)\underset{\sim}{v} + \underset{\sim}{F} \right] =$$

$$= \sum_{i=1}^{S} \underset{\sim}{j}_i \cdot \underset{\sim}{X}_i + \rho \underset{\sim}{v} \cdot \underset{\sim}{X} + \nabla \cdot \underset{\sim}{v} \cdot \underset{\approx}{\sigma} \quad . \qquad (12)$$

In these equations, $E_h$ is the internal energy per unit mass, $\underset{\sim}{j}_E$ is the energy flux with respect to the local center of mass, and $\underset{\sim}{X}_i$ is the external force on component i.

From equation 12, using the equation of motion, equation 4, one obtains after rearranging terms:

$$E_h\left(\frac{\partial \rho}{\partial t} + \underset{\sim}{v} \cdot \nabla \rho + \rho \nabla \cdot \underset{\sim}{v}\right) + \rho\left(\frac{\partial E_h}{\partial t} + \underset{\sim}{v} \cdot \nabla E_h\right) +$$

$$+ \rho \underset{\sim}{v} \cdot \left(\frac{\partial \underset{\sim}{v}}{\partial t} + \underset{\sim}{v} \cdot \nabla \underset{\sim}{v}\right) + \frac{1}{2} v^2 \left(\frac{\partial \rho}{\partial t} + \underset{\sim}{v} \cdot \nabla \rho + \rho \nabla \cdot \underset{\sim}{v}\right) = \qquad (13)$$

$$= \sum_{i=1}^{S} \underset{\sim}{j}_i \cdot \underset{\sim}{X}_i - \nabla \cdot \underset{\sim}{j}_E + \rho \underset{\sim}{v} \cdot \underset{\sim}{X} + \nabla \cdot \underset{\sim}{v} \cdot \underset{\approx}{\sigma} + \rho \epsilon \ ,$$

where equation 7 has been used.

The first and fourth parentheses on the left hand side vanish by the equation of continuity, and the second and third can be simplified by using the Stokes' operator. After use of the identity,

$$\nabla\cdot\underset{\sim}{v}\cdot\underset{\approx}{\sigma} \equiv \underset{\sim}{v}\cdot\nabla\cdot\underset{\approx}{\sigma} + \underset{\approx}{\sigma}:\nabla\underset{\sim}{v} , \tag{14}$$

Equation 13 becomes

$$\rho\frac{dE_h}{dt} = \underset{\approx}{\sigma}:\nabla\underset{\sim}{v} + \sum_{i=1}^{s}\underset{\sim}{j_i}\cdot\underset{\sim}{X_i} - \nabla\cdot\underset{\sim}{j_E} + \rho\epsilon . \tag{15}$$

This equation is not yet in the most useful form. We substitute for $\underset{\sim}{j_E}$ :

$$\underset{\sim}{j_E} = \underset{\sim}{q}' + \sum_{i=1}^{s}\underset{\sim}{j_i}\bar{E}_i = \underset{\sim}{q} + \sum_{i=1}^{s}\underset{\sim}{j_i}\left(T_h\bar{S}_i + \mu_i\right), \tag{16}$$

where $\mu_i$ is the chemical potential, $\bar{E}_i$ and $\bar{S}_i$ are partial specific quantities, and $\underset{\sim}{q}'$ and $\underset{\sim}{q}$ are heat fluxes defined by equation 16. Note that the chemical potential is the partial specific quantity, not the partial molar quantity. We define further the nonradiative entropy flux excluding the convective flux:

$$\underset{\sim}{j_{Sh}} = \frac{\underset{\sim}{q}}{T_h} + \sum_{i=1}^{s}\underset{\sim}{j_i}\bar{S}_i \tag{17}$$

and the gradient of the chemical potential minus the effects of the external forces and the temperature gradient:

$$\nabla_T\mu_i' = \nabla\mu_i - \underset{\sim}{X_i} + \bar{S}_i\nabla T_h \tag{18}$$

After substituting the expressions for the energy flux and the entropy flux into equation 15, we obtain:

$$\rho \frac{dE}{dt} = \underset{\approx}{\sigma} : \nabla \underset{\sim}{v} + \sum_{i=1}^{s} \underset{\sim}{j}_i \cdot X_i - \nabla\left(T_h \underset{\sim}{j}_{s_h}\right) - \nabla \cdot \left(\sum_{i=1}^{s} \underset{\sim}{j}_i \mu_i\right) + \rho \epsilon . \tag{19}$$

After some manipulation and use of the identity,

$$\nabla \cdot \left(a \underset{\sim}{A}\right) = a \nabla \cdot \underset{\sim}{A} + \underset{\sim}{A} \cdot \nabla \underset{\sim}{a} , \tag{20}$$

the desired non-radiative energy transport equation is obtained:

$$\rho \frac{dE_h}{dt} = \underset{\approx}{\sigma} : \nabla \underset{\sim}{v} - T_h \nabla \cdot \underset{=}{j}_{s_h} - \underset{\sim}{q} \cdot \nabla \ln T_h - \sum_{i=1}^{s} \underset{\sim}{j}_i \cdot \nabla_T \mu_i' - \sum_{i=1}^{s} \mu_i \nabla \cdot \underset{\sim}{j}_i + \rho \epsilon . \tag{21}$$

Equation 7 is already an equation of transport for radiant energy, but needs to be put in a more useful form, such that the divergence of $\underset{\sim}{F}$ is expressed in terms of the entropy flux, $\underset{\sim}{S}$, which is defined:

$$\underset{\sim}{S} = \hat{e}_x \iint L_\nu l \, d\nu \, d\Omega + \hat{e}_y \iint L_\nu m \, d\nu \, d\Omega + \hat{e}_z \iint L_\nu n \, d\nu \, d\Omega . \tag{22}$$

From the definitions of $\underset{\sim}{F}$ and $\underset{\sim}{S}$, we find

$$\nabla \cdot \underset{\sim}{F} = \frac{\partial}{\partial x} \iint I_\nu l \, d\nu \, d\Omega + \frac{\partial}{\partial y} \iint I_\nu m \, d\nu \, d\Omega + \frac{\partial}{\partial z} \iint I_\nu n \, d\nu \, d\Omega \tag{23}$$

$$\nabla \cdot \underset{\sim}{S} = \frac{\partial}{\partial x} \iint L_\nu l \, d\nu \, d\Omega + \frac{\partial}{\partial y} \iint L_\nu m \, d\nu \, d\Omega + \frac{\partial}{\partial z} \iint L_\nu n \, d\nu \, d\Omega . \tag{24}$$

We know that (3)

$$\frac{\partial L_\nu}{\partial I_\nu} = \frac{1}{T_r} \quad . \tag{25}$$

Thus, if conditions for interchanging the order of differentiation and integration are met,

$$T_r \nabla\cdot\underset{\sim}{S} = \nabla\cdot\underset{\sim}{F} \quad . \tag{26}$$

One special case for which this is satisfied is that of a monochromatic plane wave. Although a plane wave cannot have a finite intensity (3), many photochemical experiments are performed using nearly monochromatic, nearly unidirectional radiation, so we shall consider this case from here on. One could treat the general case as a superposition of plane waves, or perhaps by defining a mean temperature.

In order to investigate the entropy production, we shall seek two partial entropy equations of the form

$$\frac{\partial}{\partial t}(\rho S_h) + \nabla\cdot\underset{\sim}{J}_{Sh} - \phi_{Sh} = 0, \tag{27}$$

and

$$\frac{\partial \tilde{S}_r}{\partial t} + \nabla\cdot\underset{\sim}{S} - \phi_{Sr} = 0, \tag{28}$$

which, when added, will give an expression for $\Phi_S = \phi_{Sh} + \phi_{Sr}$ , the entropy production density. Let us first transform equation 27 into an equation in terms of quantities we have used thus far. Using the Stokes' operator, equation 27 becomes

$$\rho\frac{dS_h}{\partial t} + S_h\frac{d\rho}{dt} - \underset{\sim}{v}\cdot\nabla(\rho S_h) + \nabla\cdot\underset{\approx}{J}_{Sh} - \phi_{Sh} = 0 . \tag{29}$$

Now

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \underset{\sim}{v}\cdot\nabla\rho = -\nabla\cdot(\rho\underset{\sim}{v}) + \underset{\sim}{v}\cdot\nabla\rho = -\rho\nabla\cdot\underset{\sim}{v} \,. \qquad (30)$$

Therefore,

$$\rho\frac{dS_h}{dt} + \nabla\cdot\left(\underset{\sim}{J}_{S_h} - \rho S_h\underset{\sim}{v}\right) - \phi_{S_h} = 0 \,. \qquad (31)$$

But $\underset{\sim}{J}_{S_h} - \rho S_h\underset{\sim}{v} = \underset{\sim}{j}_{S_h}$ , so equation 31 becomes

$$\rho\frac{dS_h}{dt} + \nabla\cdot\underset{\sim}{j}_{S_h} - \phi_{S_h} = 0 \,. \qquad (32)$$

Equation 28 and 32 can now be added to obtain a total entropy equation yielding $\Phi_S$ .

To obtain an equation of the form of equation 32, we differentiate the Gibbs' equation,

$$dE_h = T_h\,dS_h - p\,dV + \sum_{i=1}^{S}\mu_i\,dm_i \,, \qquad (33)$$

with respect to time, substitute for the volume in terms of the density, $\rho$ , and solve for $dS_h/dt$ , obtaining:

$$\rho\frac{dS_h}{dt} = \frac{\rho}{T_h}\frac{dE_h}{dt} - \frac{p}{\rho T_h}\frac{d\rho}{dt} - \frac{\rho}{T_h}\sum_{i=1}^{S}\mu_i\frac{dx_i}{dt} \,. \qquad (34)$$

We know also (3)

$$\frac{\partial\tilde{S}_r}{\partial t} = \frac{1}{T_r}\frac{\partial\tilde{E}_r}{\partial t} \,. \qquad (35)$$

Substituting equation 7 and equation 21 into equation 35 and equation 34, we obtain the two entropy equations, which we combine, obtaining:

$$\rho\frac{dS_h}{dt} + \frac{\partial\tilde{S}_r}{\partial t} = \Phi_S - \nabla\cdot\underset{\sim}{j}_{S_h} - \nabla\cdot\underset{\sim}{S} \,, \qquad (36)$$

where the entropy source $\Phi_S$ is a sum of

$$\phi_1 = \frac{1}{T_h}\left(\underset{\approx}{\sigma} + p\underset{\sim}{\mathbb{1}}\right) : \nabla \underset{\sim}{v} \quad ,$$

$$\phi_2 = -\frac{\rho}{T_h}\sum_{k=1}^{t} \Delta F_k \frac{d\lambda_k}{dt} \quad ,$$

$$\phi_3 = -\frac{1}{T_h}\sum_{i=1}^{s} \underset{\sim}{j_i} \cdot \nabla_T \mu_i' \quad ,$$

$$\phi_4 = -\frac{1}{T_h}\underset{\sim}{q} \cdot \nabla \ln T_h \quad ,$$

and

$$\phi_5 = \rho\epsilon\left(\frac{1}{T_h} - \frac{1}{T_r}\right) \quad . \qquad (37)$$

Each of these terms can be separated into a product of a "generalized force" with a "flux". We choose $\rho\epsilon$ as a flux and $T_h^{-1} - T_r^{-1}$ as a force, and split the other terms in the conventional manner.

According to the theorem of Onsager, if certain hypotheses are met (5), the entropy production is a sum of products of forces and fluxes, and the matrix of phenomenological coefficients expressing the linear dependence of the forces on the fluxes is symmetric. In an isotropic medium if the fluxes depend on the forces linearly, then scalar fluxes can only depend on scalar and tensor forces, but not on vector forces. This situation arises because, to make a scalar depend linearly on a vector, the coupling coefficient must be a vector. In an isotropic medium, there are no available vectors (in the absence of external fields) which do not depend on the vector forces. But if the coupling constant depends on the vector forces, the hypothesis of linearity is violated. There are, however, isotropic tensors, so that scalars may be isotropically coupled to tensors. This result is known in the literature as a Curie's theorem, and the usual reference is reference 6. However, the referee of the paper by Mortimer and Mazo (1) quite rightly pointed out that reference 6 does not contain the above statement.

We restrict our attention to isotropic media and assume that the relation between chemical reaction rates and the stress tensor, temperature gradient and concentration gradients are linear. We do not assume that the reaction rates are linear functions of the various $\Delta F$'s or of the radiation flux. Such assumption would restrict our considerations to physically uninteresting situations and is, in any case, unnecessary. It follows that the rates of chemical reactions will be affected only by the radiation and by the forces described by the stress tensor; the latter effect has never been experimentally demonstrated, and would be expected to be very small, if found.

## C. PHOTOCHEMICAL EFFICIENCY

Since we are dealing with reactions that will not proceed in the dark, the Gibbs free energy of the system will increase as these reactions proceed photochemically. This increase of free energy of products over reactants is in principle completely available to do work through electrochemical or other processes using the reverse reactions. We define the efficiency as follows:

$$\eta \equiv \frac{1}{\epsilon} \sum_{k=1}^{h} \Delta F_k \frac{d\lambda_k}{dt} \qquad (38)$$

Where $\eta$ is the efficiency and $\Delta F_k$ is the free energy change per unit mass of reaction $k$. Those reactions (call them reactions $h+1, h+2, \ldots, t$) which do not happen to be coupled through phenomenological coefficients with a photochemical reaction of positive $\Delta F$ are excluded from the sum for reasons we will discuss.

We require that the entropy production be non-negative, according to the second law of thermodynamics. Since the forces giving rise to $\phi_3$ and $\phi_4$ cannot influence those giving rise to $\phi_1$, $\phi_2$, and $\phi_5$, by the theorem of Curie, and since the effect of the force connected with $\phi_1$ on the chemical reactions is assumed negligible, we require the sum of $\phi_2$ and $\phi_5$ to be non-negative.

$$-\frac{\rho}{T_h} \sum_{k=1}^{t} \Delta F_k \frac{d\lambda_k}{dt} + \rho\epsilon\left(\frac{1}{T_h} - \frac{1}{T_r}\right) \geq 0 . \qquad (39)$$

However, if some, say $t-h$, of the reactions are not photochemical and are not coupled to photochemical reactions, they obey a separate inequality, and equation 39 still holds if these reactions, $h+1, \ldots, t$, are excluded from the sum.

The free energy increments of the photochemical reactions we are considering are positive, so if their $d\lambda_k/dt$ are to be positive, either $\rho\epsilon$ must be positive, or else some of the coupled reactions must have a negative product $\Delta F_\ell \, d\lambda_\ell/dt$ , in which case our nominally photochemical reactions are being driven by coupled reactions instead of photochemically. In this case we can say nothing about photochemical efficiency. It may even turn out that $\eta$ is negative.

Now from equation 39 we conclude

$$\eta = \frac{1}{\epsilon} \sum_{k=1}^{h} \Delta F_k \frac{d\lambda_k}{dt} \leq 1 - \frac{T_h}{T_r} . \quad (40)$$

This limit is the same functional form as the Carnot efficiency of a reversible heat engine operating between heat reservoirs of temperature $T_r$ and $T_h$ .

Clearly the maximum efficiency can be approached only if the (negative) free energy production due to reactions which go spontaneously ("in the dark") can be made negligible. For the case of reactions which are photochemically catalyzed, rather than driven, $\eta$ will, in general, be negative. In this case, equation 40 still holds, but tells us nothing of interest.

In a study of the production of light from thermal energy, Weinstein (7) stated in a footnote that arguments similar to his could be used to show that equation 40 is the limiting efficiency for the conversion of radiant energy into work. It can also be shown that a reversible heat engine using a black-body radiation field (photon gas) as a working fluid has the efficiency given by equation 40 if $T_r$ and $T_h$ are replaced by the upper and lower temperatures with which the radiation is equilibrated.

## D. CALCULATIONS

Let us now compare our theoretical limit with experimental average efficiencies, which may be calculated approximately from data reported in the literature. The results of such comparisons for three published studies (8, 9, 10) are given in Table I.

Rabinowitch and Wood (8) studied the dissociation of iodine gas into normal iodine atoms by visible light from a carbon arc. In order to make an approximate calculation, it was necessary to compute first the radiation temperature at their reaction vessel, and then to calculate their experimental efficiency.

Since only a crude comparison can be made, only two wavelengths of the continuous carbon arc spectrum were chosen at which to calculate the radiation temperature, the wavelength of maximum emission of the arc, and the wavelength of maximum absorption. The radiation temperatures were obtained as follows: The reported number of photons absorbed per unit volume per unit time was

## TABLE I

## COMPARISON OF EFFICIENCIES

| Reaction | $I_2 \rightarrow 2I$ | | $3O_2 \rightarrow 2O_3$ | | $2NH_3 \rightarrow N_2 + 3H_2$ | |
|---|---|---|---|---|---|---|
| Reference | 8 | | 9 | | 10 | |
| Wavelength (Å) | 5050 | 5180 | 1295 | 1470 | 1295 | 1470 |
| Approx. $T_r$ (°K) | 3450 | 3400 | 4750 | 5225 | 5400 | 5900 |
| Max. Eff. | 0.91 | 0.91 | 0.94 | 0.94 | 0.94 | 0.95 |
| Exp. Eff. | 0.45 | | 0.31 | | 0.43 | |

multiplied by the energy per photon at the wavelength of maximum absorption as an approximation to the total rate of energy absorption per unit volume. From this, the total incident intensity was calculated, using the reported mean absorption coefficient, $\alpha_L$, of 18.0 $cm^{-1} atm^{-1}$ and the given cell length of 2 cm, and the reported iodine pressure of 0.15 mm of mercury. These figures yield a transmitted intensity of 98.4% of the incident intensity, which was therefore approximated by the rate of energy absorption divided by 0.016.

From this, it was possible to get the scale on the ordinate of a graph of the spectral distribution of their carbon arc given by Rabinowitch and Wood, by the use of graphical integration. This allowed the intensity per unit wavelength interval at any given wavelength to be read directly from the given curve, and this quantity was converted to intensity per unit frequency interval for the two frequencies of interest.

This intensity was then converted to intensity per unit solid angle by assuming that the arc subtended an area of 1 square centimeter and that the incident intensity came equally from all parts of this area, which was located 16 centimeters from the reaction vessel. The radiation temperature was then calculated at the two wavelengths of interest, 5180 Å and 5050 Å by substitution into equation 2, giving 3400 and 3450 degrees Kelvin.

In order to estimate the experimental efficiency, it was assumed that it would be possible to dissociate enough iodine molecules to make the iodine atom concentration equal to the iodine molecule concentration, and it was assumed that these conditions could have been approximated by an experiment of the type done by Rabinowitch and Wood. A standard free energy change for the dissociation reaction of 28.9 kcal/mole was taken, and the standard formula used:

$$\Delta F_k = \Delta F_k^{\circ} + RT \ln Q \qquad (41)$$

where $\Delta F_k^{\circ}$ is the standard free energy change, and where $Q$ is the quotient of activities raised to the proper powers (see glossary of symbols). A quantum yield of unity was assumed, and using 55.4 kcal/einstein as the average photon energy, the average efficiency was calculated with equation 38. The theoretical limit was calculated by equation 40 assuming that the radiation temperature did not vary over the reaction vessel.

Groth (9) studied the formation of ozone from oxygen, using light in the vacuum ultraviolet from a xenon lamp with a partial pressure of Xe of 0.1 mm and a partial pressure of Ne of 20 mm. Oxygen was passed through an illuminated vessel at varying rates and the ozone production was studied as a function of this rate. The ozone formation was assumed entirely due to the two emission lines at 1295 Å and 1470 Å. In order to get the intensity per unit frequency interval, it is necessary to know both the width and the shape of these lines. The literature seems to contain no information on the width of these lines in the emission spectrum, but McLennar and Turnbull (11) reported that the extreme width of the absorption line at 1470 Å was about 5 Å at a pressure of 20 mm, including the wings of the line. Not knowing the shape of the line, we make the very rough approximation that each line may be approximated by a block of radiation 1 Å wide. This is a reasonable width, according to the work of Margenau and Watson (12). A more reasonable shape would be gaussian, but this would lead to a different radiation temperature for each frequency over the line, and we would have to take some sort of average temperature. Using a square line shape gives us effectively some sort of average temperature, and simplifies the calculations.

The assumption was made that each line was of equal intensity in photons per unit time. This is only very roughly correct, since Groth reported that 73% of the absorbed energy came from the 1470 Å line. The approximate incident radiation temperature was calculated as before from equation 2, making reasonable assumptions about the area subtended by the source and the distance from the source to the reaction vessel.

However, in this case, there is another complication, since the absorption coefficient of oxygen at the wavelengths in question is very large. The transmitted intensity was accordingly very small after the light passed through only a few millimeters of the cell. We make the very rough approximation that the mean radiation temperature was about equal to the arithmetic mean of the incident radiation temperature and room temperature.

The experimental efficiency was estimated from the reported quantum yield of about 2.0. Since no data on actual concentrations were given, the standard free change of the ozization reaction, was taken as an upper limit to the actual free energy change, and equation 38 was used, assuming equal numbers of photons absorbed from each of the two spectral lines.

The data of Wijnen and Taylor (10) were even harder to work with, since they used a reaction vessel surrounding their light source, which was a xenon lamp similar to that of Groth, except that it operated at a xenon pressure of 1.5 mm, with no other gas present. This would give sharper emission lines than would Groth's lamp, so the radiation temperature was approximated by repeating the calculations on Groth's lamp assuming a block of radiation 0.3 Å wide for each line.

In order to estimate the experimental efficiency, it was assumed that the only products of the ammonia decomposition studied were nitrogen and hydrogen, and that the free energy change could be approximated by the standard free energy change of 8.0 kcal per mole of $NH_3$. Quantum yields of from 2 to 11 were reported, so the efficiency was calculated on the basis of a quantum yield of 11, and it was again assumed that the two spectral lines had equal intensities of photons per unit time. Thus the efficiency was approximated by 11 times the standard free energy change divided by the average energy per einstein of photons at 1295 and 1470 Å.

## E. DISCUSSION

The preceding development has assumed local equilibrium in the fluid system, and also in the radiation field. If absolute equilibrium were attained, the radiation would be isotropic, no chemical reactions would occur, and the radiation temperature would be equal to the thermal temperature of the fluid. This, however, is far from the case we are interested in. In most photochemical experiments, one uses nearly unidirectional radiation of rather high radiation temperature; one should ask under what conditions the actual state of such systems can be approximated by assuming local equilibrium.

First, the radiation should not be required to be isotropic, or even nearly so, since we have assumed a nearly homogeneous, isotropic fluid. In such a fluid, the effect of an individual photon is independent of the direction from which it arrives, and since the photon-photon coupling is very weak, one could think of the radiation field as being composed of essentially independent photons. This allows us to assume anisotropy, such as the nearly unidirectional radiation we discuss.

Although the case in which the radiation temperature is only slightly higher than the thermal temperature might be of interest, it should not be necessary to assume this case in order to use local equilibrium arguments. In the discussion of systems without radiation, it is sufficient to assume that gradients of macroscopic properties are small on the scale of intermolecular distances. Therefore, we shall assume for the foregoing development that the radiation temperature does not vary significantly over distances of the order of intermolecular distances. This seems equivalent to requiring local equilibrium separately in the fluid and in the radiation field, but not requiring equilibration of the radiation with the fluid. This criterion will probably be met with sufficient exactness in typical photochemical systems.

The approximation which was introduced by neglecting forces due to reflection of radiation at discontinuities is not likely to be of importance, since most photochemical reactions are carried out in systems of sufficient size that the surface of the system is not very important.

The two assumptions mentioned above are those of basic importance to sections B and C. However, the crudity of the numerical calculations of section D should probably be emphasized again. The experiments cited were designed to investigate quantum yields or reaction kinetics, and the data necessary to calculate radiation temperatures and experimental efficiencies were incomplete and had to be augmented with reasonable estimates of many numbers. However, the comparisons of Table I are expected to be qualitatively valid.

However, it would have been more useful to compare limiting and actual efficiencies of experiments designed to maximize the photochemical efficiency, but no such experiments could be found in the literature. Instead of trying to maximize the efficiency by using the longest wavelength that would cause their reactions to proceed, for example, the investigators cited used conveniently available wavelengths. Again, they used relatively high intensities, making the limiting efficiency so high as to be experimentally indistinguishable from unity.

Still, the fact remains that the actual efficiencies were lower than the theoretical limiting efficiency, as must be the case even with experiments designed to approach this limit.

The conclusion that radiant energy cannot be fully utilized in a photochemical process is not surprising, since it has been known since the time of Planck (3) that plane waves, which one might think of as sources of pure energy without entropy, cannot have finite intensities. It has also long been realized that parallel beams of monochromatic photons do not exist, since the momentum and the position of even a single photon cannot be simultaneously specified to arbitrary exactness.

Indeed, the result here obtained might have been anticipated if one thought of radiation as a means of transferring energy between black bodies, which could be used as heat reservoirs with ordinary reversible heat engines.

# GLOSSARY OF SYMBOLS

| | |
|---|---|
| $d\underset{\sim}{A}$ | Element of area times the normal unit vector |
| $c$ | Speed of light |
| $E_h$ | Internal energy per unit mass |
| $\bar{E}_i$ | Partial specific internal energy |
| $\tilde{E}_r$ | Space density of radiant energy |
| $\underset{\sim}{F}$ | Radiation energy flux (see equation 8) |
| $\Delta F_k$ | Free energy change per unit mass of the kth reaction |
| $h$ | Planck's constant |
| $\bar{H}_i$ | Partial specific enthalpy |
| $I_\nu$ | Intensity of radiation per unit area per unit time per unit solid angle per unit frequency interval |
| $\underset{\sim}{j}_E$ | Energy flux with respect to the local center of mass |
| $\underset{\sim}{j}_i$ | Diffusion flux of component i |
| $\underset{\sim}{j}_{Sh}$ | Non-radiative entropy flux (see equation 17) |
| $k$ | Boltzmann's constant |
| $L_\nu$ | Radiant entropy intensity similar to $I_\nu$ |
| $m_i$ | Mass of component i |
| $p$ | Total pressure |
| $\underset{\sim}{q}$ | Second law heat flux |
| $\underset{\sim}{q}'$ | First law heat flux |
| $Q = \dfrac{a_A^a a_B^b \cdots}{a_C^c a_D^d \cdots}$ | Activity quotient for reaction |
| $R$ | Gas constant |
| $S_h$ | Entropy per unit mass |
| $\bar{S}_i$ | Partial specific entropy |
| $\tilde{S}_r$ | Space density of radiant entropy |

| | |
|---|---|
| $\underset{\sim}{S}$ | Radiation entropy flux (see equation 22) |
| $t$ | Time |
| $T_h$ | Thermodynamic temperature |
| $T_r$ | Radiation temperature |
| $\underset{\sim}{v}$ | Macroscopic local velocity |
| $dV$ | Element of volume |
| $x_i$ | Mass fraction of component i |
| $\underset{\sim}{X}_i$ | Force on component i due to vector fields and radiation absorption |
| $\underset{\sim}{X} = \sum_{i=1}^{s} \underset{\sim}{X}_i$ | Total force as above |
| $\underset{\approx}{\mathbb{1}}$ | Unit tensor |
| $\epsilon$ | Rate of energy absorption per unit mass |
| $\eta$ | Efficiency |
| $\lambda_k$ | Progress variable of the kth reaction |
| $\mu_i$ | Chemical potential per unit mass |
| $\nabla_T \mu_i'$ | Gradient of chemical potential in an equivalent field-free isothermal system (see equation 18) |
| $\nu$ | Frequency of radiation |
| $\rho$ | Density of matter |
| $\underset{\approx}{\sigma}$ | Total stress tensor |
| $\Phi$ | Entropy source strength |
| $d\Omega$ | Element of solid angle |

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# II. MEAN VALUES IN ENSEMBLES OF SYSTEMS OF PARTICLES WITH LONG-RANGE POTENTIALS.

## A. INTRODUCTION

### 1. Explanation of the Problem

The principal business of statistical mechanics is the task of obtaining mean values, either over an ensemble of systems, or over an interval of time. One of the fundamental postulates of statistical mechanics is that an ensemble average may be identified with an observed macroscopic variable, which is by its nature a time average.

An ensemble is an assembly of a very large number of systems, which are all described by the same numbers specifying a small number of degrees of freedom, usually macroscopic, while the remaining degrees of freedom are described by parameters distributed in a way postulated for the kind of ensemble considered. The treatise by Hill (1) contains a discussion of various ensembles and their application to statistical thermodynamics.

This work will use the canonical ensemble, in which the individual systems all have the same number of particles and composition, and are in thermal contact with the same heat reservoir.

For classical systems, the canonical distribution function, which is proportional to the density of system phase points in the 6-N dimensional phase space of the N-particle system

($\Gamma$ -space), is postulated to be

$$f^{(N)}(p_1, p_2, \cdots p_N, R_1, \cdots R_N) \propto \exp\left[-\beta H(p_1 \cdots p_N, R_1, \cdots R_N)\right], \tag{1}$$

where $\beta = 1/kT$, $H$ is the Hamiltonian of the system, the $p$'s are momenta, and the $R$'s are coordinates of the particles. $T$ is the absolute temperature, and $k$ is Boltzmann's constant. The mean value of any function of positions and coordinates can be obtained by integrating its product with the distribution function over the entire phase space:

$$\langle \alpha \rangle = \frac{\int \alpha(p_1, \cdots, p_N, R_1, \cdots, R_N) e^{-\beta H} d^3p_1 \cdots d^3p_N d^3R_1 \cdots d^3R_N}{\int e^{-\beta H} d^3p_1 \cdots d^3p_N d^3R_1 \cdots d^3R_N} \tag{2}$$

The denominator of the right hand side of equation 2 is called the partition function, $Q_N$. Many ensemble averages, such as equilibrium thermodynamic quantities, can be obtained from $Q_N$ by manipulation of its definition to give an equation of the form of equation 2. We treat those functions for which the average cannot be obtained directly from $Q_N$.

Kirkwood and his students have sometimes used the symbol $\langle \alpha ; f^{(N)} \rangle$ for a mean value, emphasizing the fact that equation 2 has the form of a scalar product on $\Gamma$-space of $\alpha$ and the normalized distribution function, $f^{(N)} \equiv Q_N^{-1} e^{-\beta H}$ . The fact is not important for this work, but the canonical ensemble is simply connected with thermodynamics by the formula

$$A = -kT \ln Q_N \tag{3}$$

where $A$ is the Helmholtz free energy, or work function.

If the function, $\alpha$, of which we require an ensemble average has as arguments the coordinates and/or momenta of only a small number of particles, say, $n$, we can, instead of equation 2, use an expression in terms of reduced distribution functions, which we define as follows:

$$f^{(n)}(p_1 \cdots p_n, R_1, \ldots, R_n) \equiv \int f^{(N)}(p_1 \cdots p_N, R_1, \cdots R_N)\, d^3p_{n+1} \cdots d^3p_N\, d^3R_{n+1} \cdots d^3R_N\,, \tag{4}$$

where $f^{(N)}$ is now the normalized distribution function, $Q_N^{-1} e^{-\beta H}$. We can similarly define reduced distribution functions, $f^{(n,m)}$, depending on $n$ coordinates and $m$ momenta, where $n \neq m$, or where either $n$ or $m$ is zero. Using $f^{(n)}$, equation 2 becomes

$$\langle \alpha(p_1 \cdots p_n, R_1 \cdots R_n) \rangle = \int \alpha(p_1 \cdots p_n, R_1 \cdots R_n)\, f^{(n)}(p_1 \cdots p_n, R_1 \cdots R_n)\, d^3p_1 \cdots d^3R_n\,. \tag{5}$$

Two very useful distribution functions are the two-particle coordinate distribution function, $f^{(2)}(R_1, R_2)$ (strictly we should write $f^{(2,0)}$), and its correlation function, defined by:

$$f^{(2)}(R_1, R_2) = g^{(2)}(R_1, R_2) f^{(1)}(R_1) f^{(1)}(R_2) \quad . \tag{6}$$

In fluid systems $g^{(2)}$ is radially symmetric, and is called the radial distribution function.

In solutions, if we can designate one of the species present as solvent, a useful distribution function depends on the coordinates and/or momenta of all the solute particles and on none of the solvent particles' coordinates or momenta.

A useful function is the equilibrium potential of mean force, $W^{(n)}$, defined as follows:

$$V^{-n} \exp\left[-\beta W^{(n)}\right] = f^{(n)}(R_1, \ldots, R_n) \quad . \tag{7}$$

The negative gradient of $W^{(n)}$ with respect to the coordinates of a particle can be shown to be equal to the ensemble mean force on that particle as a function of the positions of the other particles in the set $n$, averaged over the positions of all other particles (2).

This part of the thesis consists of an investigation of mean values in an equilibrium ensemble of systems of particles interacting with long and short range forces, and is restricted to functions depending on coordinates measured at only one time. Another, more difficult case, involving coordinates and momenta measured at more than one time, and therefore involving all $6N$ coordinates and momenta through the equations of motion, will be considered in part III of this thesis.

Due to the basic similarity between equation 2 and equation 5, the methods developed will be applicable both to gases of charged particles and to ionic solutions, in which case $f^{(N)}$ is interpreted as a reduced distribution function involving only the solute ions.

An example of a function for which we might seek an ensemble average is $\sum_{i<j} z_i z_j e^2/Dr_{ij}$, where $ez_i$ is the charge on ion $i$, $D$ is the dielectric constant, and $r_{ij}$ is the magnitude of $\underset{\sim}{r}_{ij}$, the vector separating ions $i$ and $j$. This is the potential energy of set of ions in a dielectric fluid. Another function of interest might be $e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_{ij}}$, of use in neutron scattering (3).

Still another function of interest is $\delta(r_i - R_i)\,\delta(r_j - R_j)$, the ensemble average of which is $f^{(2,0)}(R_i, R_j)$.

We shall consider only classical systems. However, for quantum-mechanical cases, ensemble averages may be written in a form formally identical with equation 2 if Wigner distribution functions are used (4) instead of the density matrix formalism. Another, equivalent formalism has been employed by Mazo and Zemach (3), using Slater sums to express the ensemble average.

In this part of the thesis, the notation of Mayer (5) will be followed as much as possible.

## 2. Survey of the Literature

The modern statistical treatment of ionic solutions began with the important work of Debye and Huckel (6), based on the use of the Poisson-Boltzmann equation, the solution of which however is known not to satisfy certain integrability requirements (7). Debye and Hückel linearized the equation, obtaining a solution satisfying these requirements, and obtained their well-known expression for the radial distribution function,

$$g^{(2)}(r_{ij}) \cong 1 - \frac{z_i z_j e^2}{DkT} \frac{e^{-\kappa r_{ij}}}{r_{ij}} \qquad (8)$$

where

$$\kappa \equiv \frac{4\pi e^2}{DkT} \sum_{i=1}^{\sigma} c_i z_i^2 \quad ,$$

$D$ is the dielectric constant of the medium, $z_i$ and $c_i$ are respectively the charge number and concentration in particles per unit volume of the ionic species $i$, $e$ is the magnitude of the charge on the electron, and $r_{ij}$ is the scalar distance between the particular ions of species $i$ and $j$ being considered.

Equation 8 has had adequate experimental verification as an exact limiting law as the concentration of electrolyte approaches zero.

In the following three decades, many attempts were made to improve on the Debye-Hückel theory, including the work of Kramers (8) and many others. Onsager (9) gives an early review, and the treatise by Harned and Owens (10) contains much information about these attempts. Probably the most fundamental contribution since that of Debye and Hückel was made by Mayer (5), who obtained expressions for the ensemble averages of the osmotic pressure of an ionic solution and the activity coefficients at that pressure, valid to the next order of approximation beyond the Debye-Hückel theory.

He assumed the potential of mean force between ions at infinite dilution to be a sum of two-body coulomb forces with hard-core repulsions, and applied cluster techniques developed for non-ideal gases (12) and extended to mixtures by McMillan and Mayer (11). Divergences in the cluster integrals were taken care of by selective resummation according to groupings of terms so as to cancel out infinities of opposite sign and give a finite approximation.

Since 1950, others have continued work with Mayer's equations. Poirier (13) has obtained numerical results and various thermodynamic relationships, and Haga (14) has carried the evaluation of contributions to those of order $\kappa^5$, whereas Mayer carried them only to order $\kappa^3$. Meeron (15) has summed some of the expressions explicitly, and has discussed the use of a single hard-core repulsive potential in a mixture of ions.

Meeron has worked on expressions for the radial distribution function and two-body potential of mean force using extensions of Mayer's technique (16), and has obtained results apparently valid to order $\kappa^2$, one order better than the Debye-Hückel result.

Some of the more recent work on radial distributions for classical fluids interacting with short-range forces is of interest to this problem, since techniques developed to treat dense systems are very similar to those developed to treat long-range forces in dilute systems. Beginning with the work of Salpeter (17), Van Leeuwen, Groeneveld, and deBoer (18), and also Rushbrooke (19), have developed a "hyperchain" approximation, which also involves selective resummations, equivalent to work of Meeron (20). Morita has also invented a "hyper-netted chain" approximation (21), which Meeron (22) has pointed out, is also equivalent to his work.

Friedman (23) has derived density expansions of distribution functions without assuming the potential to be a sum of two-body potentials, but a model for the 3-body and higher potentials is not furnished. He has also extended the Mayer theory in the same sense (24).

## B. PREPARATORY DEVELOPMENT

In order to begin work on ionic solutions, it will be necessary to lay a groundwork of more general applicability. The formalism of Mazo and Zemach (3), which holds for quantum as well as classical systems, will be generalized to multicomponent systems.

Consider first the expression of distribution functions in terms of Ursell-type cluster functions. The distribution function of the set $\underset{\sim}{N} = (N_1, N_2, \ldots\ldots, N_\sigma)$ of particles of chemical species $1, 2, \ldots, \sigma$, will temporarily be called $W_{\underset{\sim}{N}}$ instead of $f^{(\underset{\sim}{N})}$ to follow Mazo and Zemach. Since the momentum dependence is immediately separable for classical systems at equilibrium, $W_{\underset{\sim}{N}}$ is assumed to be a coordinate distribution function, and is assumed separable. That is, if the set $\underset{\sim}{N}$ is divided into the mutually exclusive subsets $\underset{\sim}{n}$ and $\underset{\sim}{N} - \underset{\sim}{n}$, which are then moved apart until their separation exceeds the range of intermolecular forces, then

$$W_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) \longrightarrow W_{\underset{\sim}{N}-\underset{\sim}{n}}(\underset{\sim}{r}^{(N-n)})\, W_{\underset{\sim}{n}}(\underset{\sim}{r}^{(n)}) \,. \tag{9}$$

The expression of $W_{\underset{\sim}{N}}$ in terms of cluster functions, $U_{\underset{\sim}{\ell}}$, proceeds by use of generating functionals and functional differentiation. The product of parametric functions $a_1(\rho_{11})a_1(\rho_{21})\cdots a_\sigma(\rho_{1\sigma})\cdots a_\sigma(\rho_{N_\sigma})$ is represented by $a_1^{(N_1)} a_2^{(N_2)} \cdots a_\sigma^{(N_\sigma)}$ or by $\underset{\sim}{a}^{(\underset{\sim}{N})}$. We will frequently use an underlined symbol with an underlined exponent to represent a product of quantities raised to various powers in this manner.

The generating functional for the $W$ functions is defined

$$G_W(\underset{\sim}{a}) = \sum_{\underset{\sim}{n}=0}^{\infty} \frac{1}{\prod_{s=1}^{\sigma} n_s!} \int \underset{\sim}{a}^{(\underset{\sim}{n})} W_{\underset{\sim}{n}}\, d\rho^{(\underset{\sim}{n})} \,, \tag{10}$$

from which expression one obtains a particular $W_{\underset{\sim}{N}}$ by functional differentiation, as in Mazo and Zemach's one-component case. (4)

$$W_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) = \frac{\delta}{\delta a_1(r_{1_1})}\frac{\delta}{\delta a(r_{2_1})}\cdots\frac{\delta}{\delta a_1(r_{N_1})}\cdots\frac{\delta}{\delta a_\sigma(r_{N_\sigma})} G_W \Big|_{\underset{\sim}{a}=0} \tag{11}$$

A generating functional for a set of $U_{\underset{\sim}{\ell}}$ functions is defined exactly as in equation 10, and the $U_{\underset{\sim}{\ell}}$ functions are uniquely defined by

$$G_W(\underset{\sim}{a}) \equiv \exp G_U(\underset{\sim}{a}) \quad . \tag{12}$$

Just as in the one-component case, equation 12 relates the $U$ and $W$ functions such that if the set $\underset{\sim}{N}$ is separated as before, the separability of the $W$ functions implies that $U_{\underset{\sim}{\ell}}$ approaches zero.

From equations 11 and 12, one finds that

$$W_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) = U_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) + \sum_{\alpha=1_1}^{N_\sigma} U_\alpha(r_\alpha)\, U_{\underset{\sim}{N}-\alpha}(\underset{\sim}{r}^{(N-\alpha)}) + \cdots$$
$$\cdots + \prod_{\alpha=1_1}^{N_\sigma} U_\alpha(r_\alpha) \quad , \tag{13}$$

where the right hand side of equation 13 is a sum over all ways of dividing the set $\underset{\sim}{N}$ into mutually exclusive clusters (not counting permutations within a given cluster as distinct). This agrees with the result of McMillan and Mayer (11), who also inverted equation 13 by combinatorial methods, obtaining

$$U_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) = W_{\underset{\sim}{N}}(\underset{\sim}{r}^{(N)}) - \sum_{\alpha=1}^{N_r} W_\alpha(r_\alpha)\, W_{\underset{\sim}{N}-\alpha}(\underset{\sim}{r}^{(\underset{\sim}{N}-\alpha)}) + \cdots$$

$$\cdots + (-1)^{N-1}(N-1)! \prod_{\alpha=1}^{N_\sigma} W_\alpha(r_\alpha) \qquad (14)$$

$$= \sum_{(\ell\{\underset{\sim}{M}\}\underset{\sim}{N})} (-1)^{\ell}(\ell-1)! \prod_{j=1}^{\ell} W_{\underset{\sim}{M}_j}(\underset{\sim}{r}^{(M_j)}),$$

where the sum is again over all distinct ways of dividing the set $\underset{\sim}{N}$ into clusters. The notation $(\ell\{\underset{\sim}{M}\}\underset{\sim}{N})$ is used to represent a division of $\underset{\sim}{N}$ into $\ell$ clusters such that $\underset{\sim}{M}_1, \underset{\sim}{M}_2, \ldots, \underset{\sim}{M}_\ell$ are the sets of particles in each of these clusters. Equation 14 can also easily be obtained by taking the logarithm of equation 12 and then applying functional differentiation.

In the previous work, we have assumed that the $W$'s and $U$'s are symmetric functions of all the coordinates of molecules of the same species. We now generalize this to separable functions $W_{\underset{\sim}{M},\underset{\sim}{N},\underset{\sim}{K}}(\underset{\sim}{r}^{(M)}, \underset{\sim}{s}^{(N)}, \underset{\sim}{x}^{(K)})$, which are symmetric functions of coordinates of molecules of the same species only if they are in the same group of arguments, as for example in $\underset{\sim}{s}^{(N)}$. Any number of groups of arguments can be taken, but three groups will be chosen for illustration. The generating functional becomes

$$G_W(\underset{\sim}{a}, \underset{\sim}{b}, \underset{\sim}{c}) =$$

$$= \sum_{\underset{\sim}{m}\geq 0}\sum_{\underset{\sim}{n}\geq 0}\sum_{\underset{\sim}{k}\geq 0} \frac{1}{\underset{\sim}{m}!\,\underset{\sim}{n}!\,\underset{\sim}{k}!} \int \underset{\sim}{a}^{(\underset{\sim}{m})}\, \underset{\sim}{b}^{(\underset{\sim}{n})}\, \underset{\sim}{c}^{(\underset{\sim}{k})}\, W_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}}\, d\underset{\sim}{\rho}^{(\underset{\sim}{m})}\, d\underset{\sim}{\sigma}^{(\underset{\sim}{n})}\, d\underset{\sim}{\xi}^{(\underset{\sim}{k})}, \qquad (15)$$

where the $b$'s and $c$'s are parametric functions similar to the $a$'s. We have used the notation $\underset{\sim}{n}! \equiv \prod_{i=1}^{\sigma} n_i!$ , which will be used from now on. We also use the notation $n \equiv \sum_{i=1}^{\sigma} n_i$ .

Similarly with the previous case,

$$W_{\underset{\sim}{M},\underset{\sim}{N},\underset{\sim}{K}} = \frac{\delta}{\delta a_1(r_1)} \cdots \frac{\delta}{\delta a_\sigma(r_{M_\sigma})} \cdots \frac{\delta}{\delta b_\sigma(s_{N_\sigma})} \cdots \frac{\delta}{\delta c_\sigma(x_{K_\sigma})} G_W \Big|_{\underset{\sim}{a}=\underset{\sim}{b}=\underset{\sim}{c}=0} \qquad (16)$$

We define also,

$$G_W(\underset{\sim}{a},\underset{\sim}{b},\underset{\sim}{c}) = \exp G_U(\underset{\sim}{a},\underset{\sim}{b},\underset{\sim}{c}) \,, \qquad (17)$$

which again defines the $U$ functions uniquely.

The integrals of the $W$ and $U$ functions will be of interest, although the integrals of the $U$ functions will diverge formally for potentials of infinite range, due to the impossibility of separating subsets of particles to distances greater than the range of the potential.

Equation 17 can for our purposes be rewritten

$$\sum_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}\geq 0} a^{(\underset{\sim}{m})} b^{(\underset{\sim}{n})} c^{(\underset{\sim}{k})} w_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}} = \exp \sum_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}\geq 0} \underset{\sim}{a}^{(\underset{\sim}{m})} \underset{\sim}{b}^{(\underset{\sim}{n})} \underset{\sim}{c}^{(\underset{\sim}{k})} u_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}} \,, \qquad (18)$$

where the parametric functions have been replaced by constants, $a_1, \cdots a_\sigma, b_1, \cdots b_\sigma, c_1, \cdots c_\sigma$, and where we define

$$w_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}} = \frac{1}{\underset{\sim}{m}!\underset{\sim}{n}!\underset{\sim}{k}!}\int W_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}}(\underset{\sim}{r}^{(\underset{\sim}{m})}, \underset{\sim}{s}^{(\underset{\sim}{n})}, \underset{\sim}{x}^{(\underset{\sim}{k})}) d^{3m}\underset{\sim}{r}\, d^{3n}\underset{\sim}{s}\, d^{3k}\underset{\sim}{x}$$

(19)

$$u_{m,n,k} = \frac{1}{\underset{\sim}{m}!\underset{\sim}{n}!\underset{\sim}{k}!}\int U_{\underset{\sim}{m},\underset{\sim}{n},\underset{\sim}{k}}(\underset{\sim}{r}^{(\underset{\sim}{m})} \underset{\sim}{s}^{(\underset{\sim}{n})} \underset{\sim}{x}^{(\underset{\sim}{k})}) d^{3m}\underset{\sim}{r}\, d^{3n}\underset{\sim}{s}\, d^{3k}\underset{\sim}{x}\,.$$

In order to use the above for ensemble averages, we define $W_{0,0,\underset{\sim}{N}} = W_{\underset{\sim}{N}} = f^{(\underset{\sim}{N})}$ (strictly $f^{(\underset{\sim}{N},0)}$), the reduced coordinate distribution function of the set $\underset{\sim}{N}$ (all ions), with all configurations of the solvent averaged. All of the following will apply equally well to a gas of charged particles, in which case $f^{(\underset{\sim}{N})}$ would represent the total distribution function of the particles of the gas.

We consider first functions depending asymmetrically on the coordinates of only two particles, defining for the classical case,

$$W_{1_i,1_j,\underset{\sim}{N}-1_i1_j} = \alpha(r_{1_i}, s_{1_j}) W_{0,0,\underset{\sim}{N}} \tag{20}$$

If we require that $W_{0,0,\underset{\sim}{N}}$ be the distribution function, then $\alpha$ can depend on the coordinates of only the two particles. Note that quantum-mechanical definitions can also be made, as by Mazo and Zemach, using Slater sums.

Functions $W_{1_i,0,\underset{\sim}{M}}$ and $W_{0,1_j,\underset{\sim}{M}}$ also must exist, due to the assumed separability, by which they are defined.

A special case of separability which is of some interest is that of $W_{1_i,0,\underset{\sim}{k}} = W_{0,1_j,\underset{\sim}{k}} = 0$, corresponding to $\lim_{|r_{1_i} - s_{1_j}| \to \infty} \alpha = 0$.

From equation 18 and the above definitions, we find

$$\langle \alpha(r_{1_i}, s_{1_j}) \rangle = \frac{(\underset{\sim}{N} - 1_i 1_j)!}{\underset{\sim}{N}!} \, \frac{w_{1_i,1_j,\underset{\sim}{N}-1_i 1_j}}{w_{0,0,\underset{\sim}{N}}} \tag{21}$$

In order to express the ensemble average in terms of the $U$ integrals, we restrict $m$ and $n$ in equation 18 to $0$ or $1$. We separate all terms in the exponent independent of the $a$'s and $b$'s and expand the remaining exponential factors. Then we equate coefficients of equal powers of the $a$'s and $b$'s in the resulting expression; and obtain, for example:

$$\sum_{\underset{\sim}{N}} \underset{\sim}{c}^{\underset{\sim}{N}} w_{1_i,1_j,\underset{\sim}{N}} =$$

$$= \sum_{\underset{\sim}{k}} \left[ \underset{\sim}{c}^{\underset{\sim}{k}} u_{1_i,1_j,\underset{\sim}{k}} + \sum_{\underset{\sim}{\ell}} \underset{\sim}{c}^{\underset{\sim}{k}+\underset{\sim}{\ell}} u_{1_i,0,\underset{\sim}{k}} u_{0,1_j,\underset{\sim}{\ell}} \right] \exp \sum_{\underset{\sim}{\ell}} \underset{\sim}{c}^{\underset{\sim}{\ell}} u_{0,0,\underset{\sim}{\ell}} \,. \tag{22}$$

However, by writing equation 12 as we did equation 18, we find:

$$\sum_{\underset{\sim}{\ell}} \underset{\sim}{c}^{\underset{\sim}{\ell}} w_{0,0,\underset{\sim}{\ell}} = \exp \sum_{\underset{\sim}{\ell}} \underset{\sim}{c}^{\underset{\sim}{\ell}} u_{0,0,\underset{\sim}{\ell}} \,, \tag{23}$$

and by equating coefficients of $\underset{\sim}{c}^{\underset{\sim}{N}}$ in equation 22 after substituting equation 23, we find

$$w_{1_i,1_j,\underset{\sim}{N}} = \sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-1_i1_j} \left( u_{1_i,1_j,\underset{\sim}{n}} + \sum_{\underset{\sim}{m}=0}^{\underset{\sim}{n}} u_{1_i,0,\underset{\sim}{m}} u_{0,1_j,\underset{\sim}{n}-\underset{\sim}{m}} \right) w_{0,0,\underset{\sim}{N}-\underset{\sim}{n}-1_i1_j} \quad (24)$$

Equation 24 resembles a result of Mazo and Zemach, but has multicomponent (underlined) subscripts. From it and equation 21, we find

$$\langle \alpha(r_{1_i}, s_{1_j}) \rangle = \frac{1}{N_i(N_j - \delta_{ij})} \sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-1_i1_j} \left( u_{1_i,1_j,\underset{\sim}{n}} + \sum_{\underset{\sim}{m}=0}^{\underset{\sim}{n}} u_{1_i,0,m} u_{0,1_j,\underset{\sim}{n}-\underset{\sim}{m}} \right) \underset{\sim}{z}^{\underset{\sim}{n}+1_i1_j}, \quad (25)$$

where $z_i$ is the fugacity, in molecular units, of component $i$. We have used the relation (25)

$$w_{0,0,\underset{\sim}{N}-\underset{\sim}{n}} = \underset{\sim}{z}^{\underset{\sim}{n}} w_{0,0,\underset{\sim}{N}} \quad (26)$$

Equation 26 holds true only for $N >> n$, which will oblige us to consider an infinite system. When we allow the system to become infinite, however, we must allow the concentration of each species to remain finite and fixed.

Although the fugacity, $z_i$, of an ionic component, cannot be measured thermodynamically, mean fugacities related to it can, so we will consider equations 25 and 26 to be meaningful for ionic solutions. Mayer (5) and others

(13, 15) have studied the fugacity in ionic solutions under an external pressure equal to the osmotic pressure, so we can apply their results and work from equation 25. Mayer found that a relation of McMillan and Mayer (11) can be modified to hold for the Coulomb potential:

$$z_i = c_i e^{-S_i} \quad . \tag{27}$$

Here $S_i$ is given by

$$S_i = \frac{\partial S}{\partial c_i} = \left( \frac{\partial}{\partial c_i} \sum_{\underset{\sim}{n} \geq 2} B_{\underset{\sim}{n}} \underset{\sim}{c}^{\underset{\sim}{n}} \right)_{c_j \; j \neq i} . \tag{28}$$

The $B_{\underset{\sim}{n}}$ are cluster integrals having as integrands sums of all products of certain functions connected with diagrams in a specific way. The differentiation is simply a formal way to express the series desired, and although the $B$ integrals diverge for the Coulomb potential, they are considered independent of $c_i$ in the differentiation. Mayer obtained a finite approximation by a selective resummation, so we shall assume $S_i$ to be known.

Equations similar to equation 25 can be derived for functions, $\alpha$, depending on coordinates of any number of particles. For example,

$$\langle \alpha(r_{l_i}) \rangle = \frac{1}{N_i} \sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-l_i} u_{l_i,\underset{\sim}{n}} \underset{\sim}{z}^{\underset{\sim}{n}+l_i} , \tag{29}$$

and

$$
\begin{aligned}
\left\langle \alpha(r_{1_i}, s_{1_j}, x_{1_k}) \right\rangle &= \frac{1}{N_i(N_j-\delta_{ij})(N_k-\delta_{jk}-\delta_{ik})} \times \\
&\times \sum_{n=0}^{\underline{N}-1_i1_j1_k} \Big\{ \mathcal{U}_{1_i,1_j,1_k,\underline{n}} + \sum_{\underset{\sim}{m}=0}^{\underline{n}} \Big[ \mathcal{U}_{1_i,1_j,0,\underline{n}-\underline{m}} \mathcal{U}_{0,0,1_k,\underline{m}} + \\
&\quad + \mathcal{U}_{1_i,0,1_k,\underline{n}-\underline{m}} \mathcal{U}_{0,1_j,0,\underline{m}} + \mathcal{U}_{0,1_j,1_k,\underline{n}-\underline{m}} \mathcal{U}_{1_i,0,0,\underline{m}} \\
&\quad + \sum_{l=0}^{m} \mathcal{U}_{1_i,0,0,\underline{n}-\underline{m}} \mathcal{U}_{0,1_j,0,\underline{m}-\underline{l}} \mathcal{U}_{0,0,1_k,\underline{l}} \Big] \Big\} \underset{\sim}{z}^{\underline{n}+1_i1_j1_k}
\end{aligned}
\tag{30}
$$

Now that the expansions of Mazo and Zemach are extended to the multicomponent case, any result of cluster theory can in principle be obtained. In the following, we shall extend the applicability of this formalism to the case of the Coulomb potential.

## C. TREATMENT OF TWO-BODY FUNCTIONS

For the case of long-range potentials, the expressions such as equation 25 and 29 are not directly useful, since almost every $\mathcal{U}$ integral diverges. The intermolecular potential in a gas of charged particles and the interionic potential of mean force at infinite dilution in an ionic solution are of infinite range, so we must seek a selective resummation of the terms in such expressions, to get a finite approximation to $\langle \alpha \rangle$ . For this, it is almost imperative to connect the $u$ integrals or their integrands with cluster diagrams. In order to do this using elementary techniques, we restrict ourselves to classical systems.

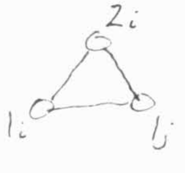
In the following, we treat explicitly the case of equation 25. The extension to mean values of functions depending on different numbers of coordinates, such as the cases of equation 29 or 30, is straightforward.

Consider first the well-known connection of Mayer's reducible cluster diagrams with his cluster integrals, $b_{\underset{\sim}{n}}$ (which are $V^{-1}$ times our $u_{0,0,\underset{\sim}{n}}$). (11)

The potential energy, or potential of mean force in the solution case, is assumed given by a sum of two-body potentials, $\varphi_{ij}(r_{1_i 1_j})$, dependent only on $|r_{1_i 1_j}|$ . The functions $f_{ij}$ are defined by

$$f_{ij}(r_{1_i 1_j}) = e^{-\beta \varphi_{ij}(r_{1_i 1_j})} - 1 \ . \qquad (31)$$

The integrands of the $b_{\underset{\sim}{n}}$ are sums of products of $f$ functions, and each term corresponds to a cluster diagram having $n$ labelled vertices representing the set $\underset{\sim}{n}$ . A line between two vertices, $1_i$ and $1_j$ , represents an $f$ function, having as argument $r_{1_i 1_j}$ . For example,



$$\longrightarrow f_{ii}(r_{1_i 2_i}) f_{ij}(r_{1_i 1_j}) f_{ij}(r_{2_i 1_j}) \ . \qquad (32)$$

The integrand of $\mathcal{U}_{0,0,\underset{\sim}{n}}$ is known (12) to consist of the sum of all products of $f$ functions corresponding to "at least singly connected" (ALSC) diagrams on the set of vertices $\underset{\sim}{n}$ . ALSC diagrams are those in which every vertex is connected to every other vertex either by a line or by a path of lines and vertices. The above statement about $U_{0,0,\underset{\sim}{n}}$ is equivalent to equation 14, as can be seen by writing the $W$ 's as products of factors for any particular set $\underset{\sim}{N}$ .

We now take the logarithm of equation 17, and by functional differentiation we find

$$U_{1_i,1_j,\underset{\sim}{N}-1_i1_j} = W_{1_i,1_j,\underset{\sim}{N}-1_i1_j} - \frac{2!}{2}\sum_{\underset{\sim}{n}=1}^{\underset{\sim}{N}-1_i1_j}\sum_{P} W_{0,0,\underset{\sim}{n}} W_{1_i,1_j,\underset{\sim}{N}-\underset{\sim}{n}-1_i1_j} \tag{33}$$

$$- \frac{2!}{2}\sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-1_i1_j}\sum_{P} W_{1_i,0,\underset{\sim}{n}} W_{0,1_j,\underset{\sim}{N}-\underset{\sim}{n}-1_i1_j} + \cdots ,$$

where $\Sigma'_P$ means a sum over the distinct ways of permuting arguments of the set $\underset{\sim}{N}-1_i1_j$ between the different $W$ functions in a product, and where the limits on the other sum mean summation over all possible sets of numbers $n_1, n_2, n_3, \ldots, n_\sigma$ up to $N_1, N_2, N_3, \ldots, N_i-1, \ldots, N_j-1, \ldots, N_\sigma$.

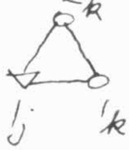
Comparison of equation 33 with equation 14 shows that a similar cluster correspondence would obtain for functions, $\alpha = a_i a_j$ , that are products of one-body functions. An equation for $U_{0,1_j,\underset{\sim}{m}}$ or $U_{1_i,0,\underset{\sim}{\ell}}$ analogous with equation 33 can be obtained:

$$U_{0,1_j,\underset{\sim}{N}-1_j} = W_{0,1_j,\underset{\sim}{N}-1_j} - \frac{2!}{2} \sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-1_j-1} W_{0,1_j,\underset{\sim}{n}} W_{0,0,\underset{\sim}{N}-\underset{\sim}{n}-1_j} . \tag{34}$$

Comparison of this with equation 14 shows that $U_{0,1_j,\underset{\sim}{N}-1_j}$ consists of the sum of all products of $f$ functions corresponding to all ALSC diagrams on the set $\underset{\sim}{N}$ of vertices, multiplied by $a_j$, where:

$$\alpha(r_{1_i}, r_{1_j}) \xrightarrow[r_{1_i1_j} \to \infty]{} a_i(r_{1_i}) a_j(r_{1_j}) \;\; .. \tag{35}$$

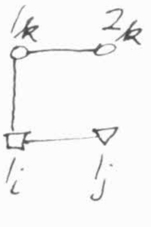
In the cluster diagrams for $U_{0,1_j,\underset{\sim}{n}-1_j}$, we use a triangle instead of a circle for the particle $1_j$:
For example

$a_j \times$


$$\Longrightarrow a_j(r_{1_j}) f_{jk}(r_{1_j1_k}) f_{kk}(r_{1_k2_k}) f_{jk}(r_{1_j2_k}) . \tag{36}$$

For the terms in $U_{1_i,0,\underset{\sim}{n}-1_i}$, which are similar, we choose to use a square for particle $1_i$.

If $\alpha \equiv a_i a_j$, then $U_{1_i,1_j,\underset{\sim}{n}-1_i1_j}$ is a sum of all products corresponding to ALSC diagrams on the set $\underset{\sim}{n}$, such as, for $\underset{\sim}{n} = 1_i1_j2_k$ for example:

$\alpha \times$


$$\Rightarrow \alpha(r_{1_i}, r_{1_j}) f_{ij}(r_{1_i1_j}) f_{ik}(r_{1_i1_k}) f_{kk}(r_{1_k2_k}) . \tag{37}$$

If $\alpha \neq a_i(r_{l_i})a_j(r_{l_j})$ for finite $r_{l_i l_j}$, some of the products corresponding to disconnected graphs survive in equation 33. If, for a particular $U_{0,0,\underset{\sim}{n}}$, equation 14 is written in diagram form, it is seen that all less than singly connected (LTSC) diagrams cancel. (Note that an ALSC diagram on the set $\underset{\sim}{n}-\underset{\sim}{m}$ multiplied by an ALSC diagram on $\underset{\sim}{m}$ is equivalent to one LTSC diagram on $\underset{\sim}{n}$.)

If equation 33 is written in diagram form for a particular $\underset{\sim}{N}$, it is seen that all LTSC diagrams that would become ALSC by addition of a line between $l_i$ and $l_j$ survive. We call these diagrams LTSC (1) diagrams. These survive in pairs, one diagram with positive sign multiplied by $\alpha$, and one with negative sign multiplied by $a_i a_j$. In order to see that this is true in general, let us see how the cancellation of diagrams arises in equation 14.

Consider a LTSC diagram which must cancel out in equation 14. It is made up of, say, $N$ disconnected ALSC pieces. This diagram will occur, with coefficient $(-1)^{M-1}(M-1)!$ a certain number of times, say $\chi_N^M$, in a sum in equation 14 having as terms products of $M$ $(M = 1, 2, \cdots, N)$ $W$ functions. The factor $\chi_N^M$ is not in general unity, since the $N$ pieces can come from $M$ clusters in a number of ways equal to the number of ways of putting $N$ distinguishable balls in $M$ identical boxes, which is

$$\chi_N^M = \sum_{\{a\}} \frac{N!}{\prod_{\alpha=1}^{M} a_\alpha! \prod_{a=1}^{N} b_a!} \quad . \qquad (38)$$

Here $a_\alpha$ is the number of balls in box number $\alpha$, $b_a$ is the number of boxes containing $a$ balls, and the sum is over all sets of occupation numbers.

We know from equation 14, that

$$\sum_{M=1}^{N}(-1)^{M-1}(M-1)!\,x_N^M = 0 \quad , \tag{39}$$

since the LTSC diagrams cancel in equation 14.

In equation 33, exactly the same diagrams occur, except that particles $l_i$ and $l_j$ are represented by a square and a triangle, respectively, and some of the diagrams are multiplied by $\alpha$ while others are multiplied by $a_i a_j$ .

The following cases occur:

(a) Particles $l_i$ and $l_j$ are in the same ALSC diagram piece. Since $l_i$ and $l_j$ are arguments of the same $W$ function, all these diagrams are multiplied by $\alpha$ , and they cancel just as in equation 14.

(b) Particles $l_i$ and $l_j$ are in different ALSC pieces say piece $A$ and piece $B$ , and $N \geq 3$. All terms in which $A$ and $B$ arose from the same $W$ will be multiplied by $\alpha$ , and all others will be multiplied by $a_i a_j$ . Single out those multiplied by $\alpha$ . In these, $A$ and $B$ ,together can be considered one piece, and we have the same cancellation as in case a) except that we now have $N-1$ "pieces".

In other words the LTSC diagram is multiplied by

$$\alpha\sum_{M=1}^{N-1}(-1)^{M-1}(M-1)!\,x_{N-1}^M = 0 \quad . \tag{40}$$

Now look at the terms multiplied by $a_i a_j$ : These have a coefficient

$$a_i a_j \left[ \sum_{M=1}^{N} (-1)^{M-1} (M-1)! \, X_N^M - \sum_{M=1}^{N-1} (-1)^{M-1} (M-1)! \, X_{N-1}^M \right],$$

but both sums here are zero, so these cancel also.

c) The last case, that of LTSC (1) diagrams is different. Here for each diagram, a nonzero coefficient $\alpha - a_i a_j$ remains.

We have therefore shown that $U_{1_i, 1_j; \underset{\sim}{N}-1_i-1_j}$ corresponds to the sum of all products of $f$ functions corresponding to ALSC diagrams multiplied by $\alpha$, plus all products corresponding to LTSC (1) diagrams multiplied by $\alpha - a_i l_j$ .

If we desire, we can connect diagrams with the $\mathcal{U}$ integrals instead of their integrands, the $U$ functions. If we do so, the diagrams are similar, but we denote only the chemical species of each particle without labelling them as though distinguishable. Of course, after integration, many terms in a given $U$ may make equal contributions, so each distinct diagram enters with a combinatorial coeffieient, which is equal to the number of permutations of vertices of the same chemical species which leave the term unchanged after integration. Finding this coefficient for the general case is a difficult combinatorial problem, which is not yet solved.

We now return to equation 25, which expresses the mean value of $\alpha$ as a series, and note that the double sum is equivalent to a sum of LTSC (1) diagrams. However, the combinatorial coefficients in the integrands here are not the same as in the $\mathcal{U}_{l_i, l_j, \underset{\sim}{n}}$ since permutations between the disconnected parts are not allowed in the $\mathcal{U}_{l_i, 0, \underset{\sim}{m}} \mathcal{U}_{0, l_j, \underset{\sim}{n}-\underset{\sim}{m}}$ product diagrams. The ratio of the coefficients of a particular LTSC (1) diagram in $\mathcal{U}_{l_i, 0, \underset{\sim}{m}} \mathcal{U}_{0, l_j, \underset{\sim}{n}-\underset{\sim}{m}}$ and in $\mathcal{U}_{l_i, l_j, \underset{\sim}{n}}$ must then be $\frac{\underset{\sim}{m}!(\underset{\sim}{n}-\underset{\sim}{m})!}{\underset{\sim}{n}!}$. This is the inverse of the ratio of the factors in front of the integrals, so the double sum cancels exactly the LTSC (1) diagrams in the single sum with coefficient $-a_i a_j$. Now if we define $\mathcal{U}'_{l_i, l_j, \underset{\sim}{n}}$ as being like $\mathcal{U}_{l_i, l_j, \underset{\sim}{n}}$ except for deleting the terms multiplied by $-a_i a_j$, its integrand contains all products corresponding to ALSC and LTSC (1) diagrams, all multiplied by $\alpha$, and equation 25 becomes

$$\left\langle \alpha(r_i, r_j) \right\rangle = \frac{1}{N_i(N_j-\delta_{ij})} \sum_{\underset{\sim}{l}=0}^{\underset{\sim}{N}-l_i l_j} \mathcal{U}'_{l_i, l_j, \underset{\sim}{l}} \, \underset{\sim}{z}^{\underset{\sim}{l}+l_i l_j} . \tag{41}$$

We neglect $\delta_{ij}$ compared with $N_j$ and define:

$$I_{\underset{\sim}{l}}^{ij} \equiv V^{-2} \mathcal{U}'_{l_i, l_j, \underset{\sim}{l}} . \tag{42}$$

Equation 41 becomes, using equation 27:

$$\left\langle \alpha(r_i, r_j) \right\rangle = \sum_{\underset{\sim}{l}=0}^{\underset{\sim}{N}-l_i l_j} I_{\underset{\sim}{l}}^{l_i l_j} \underset{\sim}{c}^{\underset{\sim}{l}} \left(1 - \sum_t l_t^* S_t + \cdots \right) , \tag{43}$$

where we use $l_t^* = l_t + \delta_{it} + \delta_{jt}$ .

Equation 43 is now a density expansion, at least formally, but it is not in the most convenient form. However, we shall work first with this form, as do Mazo and Zemach (3).

We begin by expanding the $f$ functions, following Mayer (5), assuming the potential of mean force at infinite dilution to be the Coulomb potential with a dielectric constant plus a repulsion at short range:

$$f_{ij}(r_{l_i l_j}) = k_{ij}(r_{l_i l_j}) + \sum_{n=1}^{\infty} \frac{1}{n!} \left[ -\lambda z_i z_j g(r_{l_i l_j}) \right]^n \left( k_{ij}(r_{l_i l_j}) - 1 \right), \tag{44}$$

where

$$\lambda = \frac{4\pi\epsilon^2}{DkT}$$

and

$$g_{ij}(r_{l_i l_j}) = \frac{e^{-\alpha r_{l_i l_j}}}{4\pi\, r_{l_i l_j}}$$

Here $D$ is the dielectric constant of the medium, $\epsilon$ is the magnitude of the electron's charge, $k$ is Boltzmann's constant, and $T$ is the temperature. The parameter $\alpha$ will later be allowed to approach $0$. The function $k_{ij}$ is similar to $f_{ij}$ except that only the short-range repulsive potential $w^*$ is included:

$$k_{ij}(r_{l_i l_j}) = \exp\left(-w_{ij}^*(r_{l_i l_j})/kT\right) - 1 \quad .$$

If this repulsive potential is that of hard spheres,

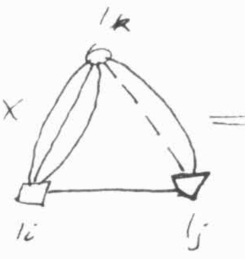
$$k_{ij}(r_{1_i1_j}) = \begin{cases} -1 & r_{1_i1_j} < a_{ij} \\ 0 & r_{1_i1_j} > a_{ij} \end{cases} , \tag{45}$$

where $a_{ij}$ is the distance of closest approach of ions of species $i$ and $j$.

Each term in a given $I^{ij}_{\underset{\sim}{n}}$ is now replaced by an infinite number of terms, each of which we associate with another type of diagram, in which a solid line between two vertices, say $k$ and $\ell$, represents $g(r_{k\ell})$. A broken line will represent a $k$ function, two solid lines will represent $\frac{1}{2!}g^2(r)$, one broken and one solid line will represent $k(r)g(r)$, etc.

For example,

$\alpha \times$



$$\Longrightarrow \alpha(r_{1_i}, r_{1_j}) \frac{\left[g(r_{1_i1_k})\right]^3}{3!} g(r_{1_i1_j}) g(r_{1_j1_k}) k(r_{1_j1_k}). \tag{46}$$

We shall call $I^{ij}_{\underset{\sim}{\ell}}(\eta)$ the term in $I^{ij}_{\underset{\sim}{\ell}}$ corresponding to the diagram $\eta$. The contribution to $\langle\alpha\rangle$ from $\eta$ is

$$I^{ij}_{\underset{\sim}{\ell}(\eta} \; \underset{\sim}{\varsigma}^{\underset{\sim}{\ell}} \exp\Big(-\sum_t \ell_t^* S_t\Big) . \tag{47}$$

A row of vertices, each connected only by two solid lines, is called a chain. If a diagram contains no chains, except possibly chains composed entirely of the particles $1_i$ and $1_j$, it is called a prototype diagram. A diagram, $\eta$, will be said to belong to a prototype, $\zeta$, if it becomes identical to $\zeta$ upon replacing all chains (excluding those containing particles $1_i$ and $1_j$) by lines. We shall later use a prototype diagram to represent the sum of all diagrams belonging to it, in which case we shall draw it with wiggly lines. A typical diagram and its prototype are:

(48)

Note that $1_i$ and $1_j$ remain, even if contained in chains in the diagram. In the set $\underset{\sim}{\ell}^*$, we call the vertices in the chains $\underset{\sim}{n}$, and the other vertices $\underset{\sim}{m}^*$. Expression 47 becomes

$$I^{ij}_{\underset{\sim}{\ell}(\eta)}\, \underset{\sim}{\zeta}^{\underset{\sim}{\ell}} \exp\left(-\sum_t m^*_t \zeta_t\right)\left[1-\sum_t n_t \zeta_t + \cdots\right] . \qquad (49)$$

Mayer has shown (5), for the case of the irreducible cluster integrals, that a sum of the form $B_{\underset{\sim}{n}}\, \underset{\sim}{\zeta}^{\underset{\sim}{n}}$ is replaced by a sum of the original form including only prototype diagrams, and that in these, instead of $g$ functions, the solid lines, which we now draw "wiggly" following Salpeter, represent

$$g^{(0)}(r) = \frac{e^{-\kappa r}}{4\pi r} \tag{50}$$

Mayer's proof of this (5) is included in Appendix 1.

The theorem holds true also in our case for the contribution in equation 49 independent of $\sum_t n_t S_t$ . The only differences are that our definition of prototypes must be used and that all integrands are multiplied by $\alpha(r_{1_i}, r_{1_j})$. This doesn't affect the "chain-shrinking" since $1_i$ and $1_j$ are never in the set $\underset{\sim}{n}$ . The contribution of a prototype, $\zeta$ , we write

$${}^{o}I^{ij}_{m(\zeta)} \underset{\sim}{C}^{\underset{\sim}{m}} \tag{51}$$

The contributions from the further terms in the series in expression 49 are slightly more complicated. For these, we restrict ourselves to the case $|z_1| = |z_2| = \cdots |z_\sigma|$. For this case $S_1 = S_2 = \cdots S_\sigma$ . The sum in the bracket in equation 49 now becomes

$$\sum_t n_t S_t = S_1 n = S_1 \sum_{\alpha=1}^{\nu} n_\alpha \quad , \tag{52}$$

where we number the chains in $\eta$ from $1$ to $\nu$ , and $n_\alpha$ is the number of particles in chain $\alpha$ . Consider each of the $\nu$ terms in equation 52 separately. The summation over diagrams belonging to the prototype $\zeta$ will lead to the same result as before except for chain number $\alpha$ , which is replaced by

$$g^{(1)}(r) = \sum_{n=0}^{\infty} (-\kappa^2) n g_n(r) = -\frac{\kappa}{8\pi} e^{-\kappa r} \quad . \tag{53}$$

The contributions multiplied by $S_1{}^2 \sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu} n_\alpha n_\beta$ give us $\nu^2$ terms in expression 49. Summation over diagrams belonging to a prototype, $\zeta$ , gives a result similar to the previous case except that chain $\alpha$ and chain $\beta$ are replaced by $g^{(1)}(r)$ instead of $g^{(0)}(r)$ if $\alpha \neq \beta$ . If $\alpha = \beta$ , this chain must be replaced by

$$g^{(2)}(r) = \sum_{n=0}^{\infty} (-\kappa^2) n^2 g_n(r) = \frac{\kappa e^{-\kappa r}}{16\pi} (\kappa r - 1) \tag{54}$$

in summing over the diagrams.

The contribution from the $S_1{}^3$ sum is similar. There are $\nu(\nu-1)(\nu-2)$ terms with different combinations of three chains replaced by $g^{(1)}(r)$ instead of $g^{(0)}(r)$ , $3\nu(\nu-1)$ terms with one chain replaced by $g^{(1)}(r)$ and one by $g^{(2)}(r)$ , and $\nu$ terms, each with one chain replaced by

$$g^{(3)}(r) = \sum_{n=0}^{\infty} (-\kappa^2) n^3 g_n(r) = \frac{\kappa e^{-\kappa r}}{32\pi} (-\kappa^2 r^2 + 3\kappa r - 1) \quad . \tag{55}$$

Before we can express all orders of contributions to $\langle \alpha \rangle$, we need an expression for $g^{(p)}(r)$, which is defined:

$$g^{(p)}(r) = \sum_{n=0}^{\infty} (-\kappa^2) n^p g_n(r) \quad , \tag{56}$$

and which we seek as follows.

First, we note that

$$g^{(p)}(r) = \left( \frac{\kappa}{2} \frac{\partial}{\partial \kappa} \right)^p g^{(0)}(r) \quad , \tag{57}$$

where $g^{(0)}(r)$ is given by equation 50. Since $r$ occurs in the exponent of $g^{(0)}(r)$ in the product $\kappa r$ we can write $g^{(p)}(r)$ conveniently as a polynomial in $-\kappa r$ times $e^{-\kappa r}$ :

$$g^{(p)}(r) = P_p(-\kappa r) \frac{e^{-\kappa r}}{4\pi r} = \frac{1}{2^p} \sum_{s=0}^{p} C_p^s (-\kappa r)^s \frac{e^{-\kappa r}}{4\pi r} \quad . \tag{58}$$

By operating on equation 58 with $\frac{\kappa}{2}\frac{\partial}{\partial \kappa}$, we obtain the recursion relation

$$C_{p+1}^{s} = s\, C_p^s + C_p^{s-1} \tag{59}$$

by equating equal powers of $r$.

By inspection of a few special cases, we concluded that the following was probably the correct expression for $C_p^s$:

$$C_p^s = \sum_{t=0}^{s} \frac{t^p (-1)^{t-s}}{t!(s-t)!} \tag{60}$$

Equation 60 can be proved by induction, but since the proof is slightly tedious, it is relegated to the Appendixes (Appendix 2).

Now that we have $g^{(p)}(r)$, we can find the contributions of higher order than $S_1^3$, simply by proceeding in an analogous manner, with obvious results.

In order to write the contribution of a given prototype $\zeta$, we introduce left subscripts, as well as left superscripts, on $I_{\underset{\sim}{m}(\zeta)}^{(j)}$. If $\zeta$ has $\nu$ chains, there are $\nu$ left subscripts, and if the contribution is to be multiplied by $S_1^p$, we affix a left superscript $p$. If the $\alpha^{\underline{th}}$ left subscript is $p_\alpha$, this means that after summation the $\alpha^{\underline{th}}$ chain is replaced by $g^{(p_\alpha)}(r)$. It is apparent that a given set of left subscripts can arise more than once in the $\nu^p$ terms multiplied by $S^p/p!$. Since we have $p$ sums $\sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu} \cdots \sum_{\omega=1}^{\nu}$ multiplied together, the coefficients will be the multinomial coefficients:

$$\frac{p!}{\prod_{\alpha=1}^{\nu} p_\alpha !} \quad . \tag{61}$$

Thus the contribution of a given prototype $\zeta$ to $\langle \alpha \rangle$ is

$$\underset{\sim}{c}^{\underset{\sim}{m}} e^{-m^* S_1} \Big[ {}^{0}I^{ij}_{\underset{\sim}{m}(\zeta)} - S_1 \sum_{\substack{\{p_\alpha\} \\ \sum_\alpha p_\alpha = 1}}' {}^{1}_{\{p_\alpha\}}I^{ij}_{\underset{\sim}{m}(\zeta)} + S_1^2 \sum_{\substack{\{p_\alpha\} \\ \sum_\alpha p_\alpha = 2}}' \frac{1}{\prod_\alpha p_\alpha!} \, {}^{2}_{\{p_\alpha\}}I^{ij}_{\underset{\sim}{m}(\zeta)} - + \cdots \Big], \tag{62}$$

where the sums are over all sets of left subscripts consistent with $\sum_\alpha p_\alpha = p$ .

Now in order to obtain an approximation to a given $\langle \alpha \rangle$ to any order in $\kappa$ , we simply need to sum expression 62 over whatever $\underset{\sim}{m}$ and $\zeta$ necessary. However, it is very difficult to determine, _a priori_, which prototypes must be considered, and it may be difficult to determine how many terms of the series in square brackets in equation 57 to take. As a matter of fact, consideration of the form of expression 57 leads one to conclude that an infinite subset of prototypes should be taken immediately to cancel the expression $\exp(-m^* S_1)$ .

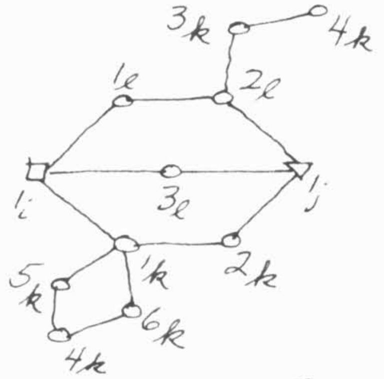
However, this can in effect be accomplished more easily by returning to equation 41 and deriving a more useful density expansion, as suggested by the work of Meeron (16) and of Salpeter (17). We shall use the method of Salpeter, which is illustrated in Appendix 3, where it is extended to the multicomponent case.

We write equation 41 in the form

$$\langle \alpha(r_{1_i}, r_{1_j}) \rangle = \sum_{\underset{\sim}{n}=0}^{\underset{\sim}{N}-1_i1_j} I_{\underset{\sim}{n}}^{ij} \underset{\sim}{c}^{\underset{\sim}{n}} \underset{\sim}{\gamma}^{\underset{\sim}{n}+1_i1_j} \tag{63}$$

and recall that the integrand of $I_{\underset{\sim}{n}}^{ij}$ contains all products of $f$ functions corresponding to ALSC and LTSC (1) diagrams, including those containing articulation points. (An articulation point is a vertex at which the diagram may be severed into disconnected parts by breaking all the lines drawn to that vertex.)

Consider now an ALSC diagram representing a term in the integrand of $I_{\underset{\sim}{n}}^{ij}$ in equation 63, say the diagram $\xi$:



In this diagram, vertices $1_k$ and $2_l$ are articulation points, and the parts of the diagram attached to the set $\underset{\sim}{k}^* = (1_i, 1_j, 1_k, 2_k, 1_l, 2_l, 3_l)$ only at those points will be called appendages. The set $\underset{\sim}{k}^*$ constitute an "at least doubly connected," ALDC, diagram (unless there is only one chain connecting $1_i$ and $1_j$ ) or an "irreducible diagram".

An ALDC diagram contains at least two independent paths leading between any two vertices.

We call the set of particles in the appendage attached at vertex $\mu_s$ the set $\underset{\sim}{\ell}(\mu_s)$, and this set may be of any size (or empty) and connected among its own members in any conceivable way, but can be attached to no other member of $\underset{\sim}{k}^*$ except $\mu_s$ .

When the integration in $I^{ij}_{\underset{\sim}{n}}$ is performed, integration in turn over the coordinates of particles represented by appendage vertices gives factors multiplying the contribution obtained by integrating over the coordinates of the set $\underset{\sim}{k}^*$. Of course, since $\xi$ must contain the vertex set $\underset{\sim}{n}^*$, we can write

$$\underset{\sim}{n}^* = \underset{\sim}{n} + i, j = \underset{\sim}{k}^* + \sum_{\mu_s = 1}^{\underset{\sim}{n}} \underset{\sim}{\ell}(\mu_s) \quad . \tag{64}$$

The LTSC (1) diagrams are treated in exactly the same way, except of course for the fact that $\underset{\sim}{k}^*$ contains only $i$ and $j$, and there is no irreducible diagram.

The contribution of $\xi$ to equation 63 can be written

$$\frac{1}{V^2}\frac{1}{\underset{\sim}{n}!}\int\left(\prod_{irred.} f\right)\alpha(r_i, r_j)\, d^3_r{}^{(\underset{\sim}{k}^*)} \prod_{\mu_s=1}^{\underset{\sim}{k}^*}\left\{\int\left(\prod f\right) d^3_r{}^{(\underset{\sim}{\ell}(\mu_s))}\, \underset{\sim}{z}^{\underset{\sim}{\ell}(\mu_s)}\right\} \tag{65}$$

$$\times\, \underset{\sim}{c}^{\underset{\sim}{k}}\, \underset{\sim}{\gamma}^{\underset{\sim}{k}^*} \quad .$$

The first $(\Pi f)$ must correspond to an ALDC diagram, unless there are fewer than two paths from $l_i$ to $l_j$ ; and the others correspond to ALSC appendages. In the case of the LTSC (1) diagrams, instead of the ALDC contribution we have simply $\int \alpha(r_{1i}, r_{1j})\, d^3r_{1i}\, d^3r_{1j}$ .

Since we have till now regarded the particles as distinguishable, we must now multiply expression 65 by the number of ways to pick the sets $\underset{\sim}{k}, \underset{\sim}{l}(1), \ldots, l(k_\sigma^*)$ from the set $\underset{\sim}{n}$ ;

$$\frac{\underset{\sim}{n}!}{\underset{\sim}{k}!\prod_{\mu_s=1}^{k_\sigma^*}\underset{\sim}{l}(\mu_s)!}$$

giving

$$\frac{1}{V^2}\frac{1}{\underset{\sim}{k}!}\int_{\substack{\text{ALDC}\\ \text{on } \underset{\sim}{k}^*}}(\Pi f)\,\alpha\, d^3r^{(\underset{\sim}{k}^*)}\prod_{\mu_s=1}^{k_\sigma^*}\left\{\frac{1}{\underset{\sim}{l}(\mu_s)!}\int_{\substack{\text{ALSC on}\\ \underset{\sim}{l}(\mu_s)+\mu_s}}(\Pi f)\, d^3r^{[\underset{\sim}{l}(\mu_s)]}\,\underset{\sim}{z}^{\underset{\sim}{l}(\mu_s)}\right\}\times \tag{66}$$

$$\times\, \underset{\sim}{c}^{\underset{\sim}{k}}\gamma^{\underset{\sim}{k}^*}$$

If we call $V^{-2}(\underset{\sim}{k}!)^{-1}$ times the first integral, $\mathcal{Q}^{ij}_{\underset{\sim}{k}(\psi)}$, where $\psi$ refers to the ALDC diagram, and call the sum over all ALDC diagrams, on $\underset{\sim}{k}^*$, $\mathcal{Q}^{ij}_{\underset{\sim}{k}}$ , and then sum expression 66 over all such $\psi$ and over all ALSC diagrams on each set $\underset{\sim}{l}(\mu_s)+\mu_s$ , we obtain

$$\mathcal{Q}^{ij}_{\underset{\sim}{k}}\prod_{\mu_s=1}^{k_\sigma^*}\left\{(l_s(\mu_s)+1)\, b_{\underset{\sim}{l}(\mu_s)+1_s}\,\underset{\sim}{z}^{\underset{\sim}{l}}\right\}\underset{\sim}{c}^{\underset{\sim}{k}}\underset{\sim}{\gamma}^{\underset{\sim}{k}^*}. \tag{67}$$

By equation A34, summing this over all $\underset{\sim}{\ell}(\mu_s)$ for each $\mu_s$ gives

$$\mathcal{L}^{ij}_{\underset{\sim}{k}}\,\underset{\sim}{c}^{\underset{\sim}{k}} \quad . \tag{68}$$

Summing expression 68 over all $\underset{\sim}{k}$ gives us a convenient density expansion for $\langle\alpha\rangle$ :

$$\langle\alpha(r_i, r_j)\rangle = \sum_{\underset{\sim}{k}=0}^{\underset{\sim}{N}-1_i1_j} \mathcal{L}^{ij}_{\underset{\sim}{k}}\,\underset{\sim}{c}^{\underset{\sim}{k}} \quad . \tag{69}$$

Now we treat this exactly as we did the term of equation 43 independent of $\sum_t n_t S_t$ ; expanding the functions, defining new diagrams and prototypes. The only difference is that only diagrams occur in which all particles lie on direct paths from $1_i$ to $1_j$ (irreducible diagrams). The chain-shrinking theorem of Mayer applies directly, and we obtain finally after summing over all diagrams belonging to the same prototype,

$$\langle\alpha(r_i, r_j)\rangle = \sum_{\underset{\sim}{m}=0}^{\underset{\sim}{N}-1_i1_j} {}^{\circ}\mathcal{L}^{ij}_{\underset{\sim}{m}}\,\underset{\sim}{c}^{\underset{\sim}{m}} \quad . \tag{70}$$

Here ${}^{\circ}\mathcal{L}^{ij}_{\underset{\sim}{m}}$ is defined as was $\mathcal{L}^{ij}_{\underset{\sim}{m}}$ , except that the integrand is a sum of products of $k$ functions and $f^{(0)}$ functions, corresponding to irreducible prototype diagrams.

In principle, the problem of obtaining a finite approximation for $\langle\alpha\rangle$ is now solved, since all the integrals will converge for functions $\alpha$ of interest.

However, we still have an infinite number of prototypes, and there is no systematic way to pick those which must be included to obtain an approximation exact to some order in the concentration. This is due to the fact that the $\overset{\circ}{\mathcal{Q}}$ functions are concentration-dependent, due to the dependence of $g^{(0)}$ on the Debye parameter, $\kappa$. Thus, one can not obtain an approximation to order $c^{n}$ just by taking all prototypes up to those for which $m=n$, since later $\overset{\circ}{\mathcal{Q}}$ functions could be proportional to high inverse powers of concentration, cancelling all or part of the factors of concentration multiplying them.

This is a general failing of cluster integral theory, and future work could well be concentrated on seeking a systematic ordering scheme. Nevertheless, one can investigate the smaller prototype diagrams individually, hope that there are no prototypes among the larger ones that behave much differently, and thus hope to order the contributions provisionally.

We illustrate the process of ordering the contributions of prototypes by considering the case of $\alpha=\delta(r_{1_i}-R_{1_i})\delta(r_{1_j}-R_{1_j})$, for which

$$\langle\alpha(r_{1_i},r_{1_j})\rangle=\langle\delta(r_{1_i}-R_{1_i})\delta(r_{1_j}-R_{1_j})\rangle\propto g^{(2)}(R_{1_i1_j})\,. \tag{71}$$

Here the $\delta$'s are three-dimensional Dirac delta functions and $g^{(2)}(r)$ is the radial distribution function or two-body correlation function.

However, as previously stated, the radial distribution function in ionic solutions has been studied by diagram techniques by Salpeter (17) and by Meeron (16), and the work of Meeron can be used directly to order the prototype contributions for the case of equation 71, and hence indirectly for general $\alpha$. Explicit expressions for contributions reducing to prototypes in a way different from simply summing over chains have also been obtained.

We shall review now some of the results of Meeron* which are applicable to the case of $\alpha = \delta(r_{1_i} - R_{1_i})\delta(r_{1_j} - R_{1_j})$. This work uses diagrams in which two points are fixed while the others are integrated over. In our scheme, these are the vertex □ and the vertex ▽, and are integrated over using the delta functions. The diagrams are otherwise equivalent. A few differences in notation are noted. We have followed the notation of Mayer, in which the chain bonds are called $q$-bonds, and the short-range bonds $k$-bonds. Meeron calls the chain-bonds $\kappa$ bonds, and the short-range bonds $f$ bonds. His $K = \lambda(4\pi)^{-1}$, but otherwise the notation is similar, except for his use of $U^*$ where we use $w^*$. Where the notation differs, we present the results in our notation.

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* See section 5 of reference (16b).

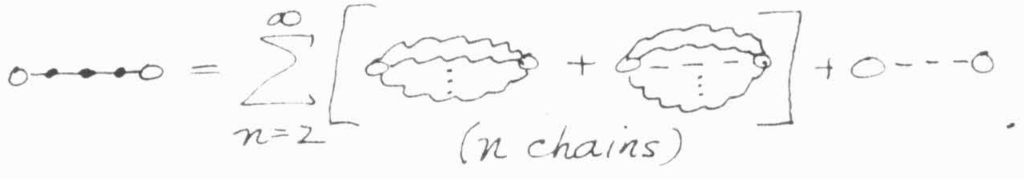
It is possible to sum over prototypes differing only in the number of chains joining pairs of vertices, and such summing over all numbers of chains (excluding unity, since that is the $q$ bond) gives the "$\psi$ bond," which represents the function

$$\psi_{ij}(r_{1_i1_j}) = F_{ij}(r_{1_i1_j}) + \lambda q^{(0)}(r_{1_i1_j}) z_i z_j \tag{72}$$

where

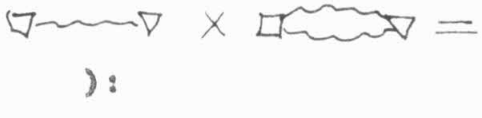
$$F_{ij}(r_{1_i1_j}) = \exp\left[-\frac{w^*(r_{1_i1_j})}{kT} - z_i z_j \lambda q^{(0)}(r_{1_i1_j})\right] - 1 .$$

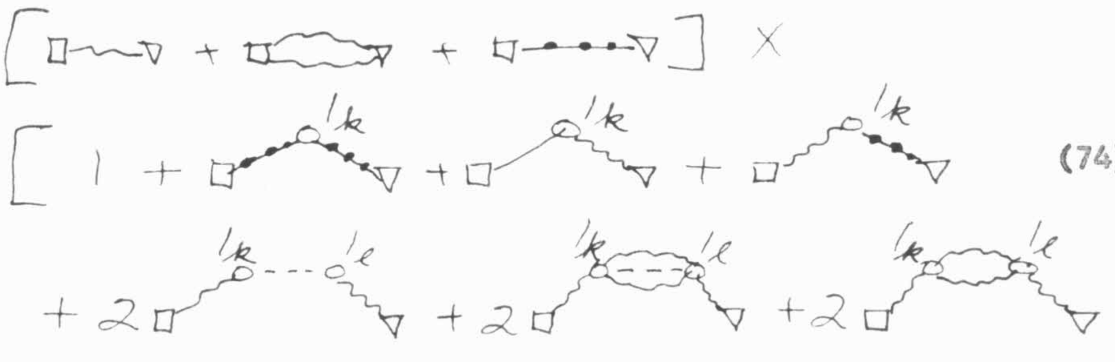
Note that $\psi$ differs from $F$ since the contribution of the $q$-bond, $-\lambda z_i z_j q^{(0)}(r)$ must be subtracted off. If we use a line —•—•—•— to represent a $\psi$ bond, then symbolically



(73)

Using $\psi$-bonds, the sum over prototypes is replaced by one of the same form, but the prototypes now have any combination of $\psi$-bonds and $q$-bonds. The $\psi$-bonds can occur in chains, whereas the $q$-bonds still cannot.

No contributions to the radial distribution function up to order $\kappa^2$ have been found, besides those of the following diagrams (for compactness, we use a product representation, as for example  ):



(74)

This corresponds to the expression, effectively factored in the same manner as the diagrammatic expression:

$$g^{(2)}(R_{1_i1_j}) = \left[F_{ij}(R_{1_i1_j}) + 1\right]\left[1 + \sum_{s=1}^{\sigma} c_s \Gamma_s(R_{1_i1_j}) + \sum_{s,t=1}^{\sigma} \frac{1}{2} c_s c_t \left\{\Gamma_{st,1}(R_{1_i1_j}) + \Gamma_{st,2}(R_{1_i1_j})\right\}\right] . \tag{75}$$

In equation 75, $\Gamma_s$ is the contribution of the first three diagrams in the second bracket, for $s = k$ ; $\Gamma_{st,1}$ is the contribution of the next diagram for $s = k$ and $t = l$ ; and $\Gamma_{st,2}$ is the contribution for the remaining two, for $s = k$ and $t = l$ .

These functions are given by:

$$\Gamma_s(R_{1_i1_j}) = \int \left[F_{is}(R_{1_i1_s}) F_{sj}(R_{1_s1_j}) - \lambda^2 z_i z_s^2 z_j q^{(0)}(R_{1_i1_s}) q^{0}(R_{1_s1_j})\right] d^3R_{1_s} \, , \tag{76}$$

$$\Gamma_{st,1}(R_{1_i1_j}) = 2\lambda^2 z_i z_s z_t z_j \iint g^{(0)}(R_{1_i1_s})\, k^*(R_{1_s1_t})\, g^{(0)}(R_{1_t1_j})\, d^3R_{1_s}\, d^3R_{1_t} \qquad (77)$$

$$\Gamma_{st,2}(R_{1_i1_j}) =$$

$$= 2\lambda^4 z_i z_s^2 z_t^2 z_j \iint g^{(0)}(R_{1_i1_s}) \exp\left[-\frac{w^*(R_{1_s1_t})}{kT}\right]\left[g^{(0)}(R_{1_s1_t})\right]^2 g^{(0)}(R_{1_t1_j})\, d^3R_{1_s}\, d^3R_{1_t}. \qquad (78)$$

The second term in the integral of equation 76 can be evaluated by the convolution theorem to obtain

$$-\lambda z_i z_j z_s^2\, e^{-\kappa R_{1_i1_j}} / 8\pi\kappa \qquad (76a)$$

but the first term must be done numerically. Equations 77 and 78 can be evaluated analytically; at least for certain specific forms of $w^*$. We now have the radial distribution function to order $\kappa^2$, and hence by using the same diagrams, any other two-body function to a similar approximation.

The Debye-Hückel radial distribution, equation 8, is obtained by ignoring the $\Gamma$'s in equation 75, and then linearizing the expression for $F$ with respect to the charges $z_i$ and $z_j$ .

## D. DISCUSSION

Although we have treated explicitly only the case of functions depending on the coordinates of two particles, the extension to other cases, such as functions depending on momenta or on other coordinates, symmetrically or unsymmetrically, is straight forward, and will not be presented. In the case of a two-body function depending on coordinates and momenta, the result of equation 70 is a function of the two momenta. Since the momenta are separable at equilibrium, multiplication of this result by the two one-particle momentum distribution functions followed by integration gives the final result.

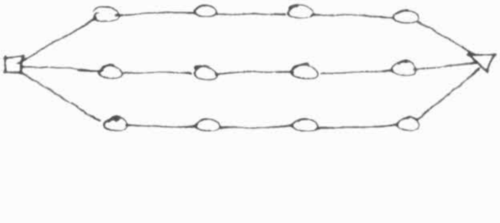
This study is subject to the limitations of cluster treatments in general. First, we assumed that the potentials involved are sums of two-body potentials. This is not strictly true, although it would be expected to hold to a much better approximation for an ionized gas than for an ionic solution. Friedman (23, 24) has attempted to avoid this limitation, and has formally included 3-body, 4-body, and higher potentials. However, his work is not of current interest, since no simple model is available for these potentials. Our work could easily be extended in the Friedman sense, if a model for the higher potentials becomes available.

Another limitation is the use of a dielectric constant to represent the solvent. Since the solvent is not a continuous fluid, but is very inhomogeneous on a molecular scale, this approximation is probably considerably in error for close ion-ion approaches. However, for sufficiently dilute solutions, such approaches are rare, and do not justify a more complicated model.

Probably a more serious shortcoming is the fact that it is impossible, as yet, to make certain the ordering of the contributions of the prototypes without investigating each one of the infinite number explicitly (16b). This occurs because series such as equation 70 are not well-ordered Taylor expansions to begin with, since the coefficients, which themselves depend on the expansion variables, are evaluated to all orders. It may be possible to remedy this situation, perhaps through a very sophisticated use of topology, and future work in this area might be fruitful.

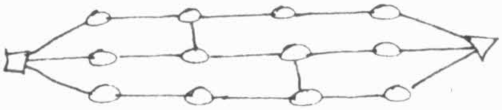
A related shortcoming, is that large classes of diagrams having cross-links between chains are ignored, or at least relegated to belong to more complicated prototypes than can be examined. For example, consider the two diagrams

(1)



(79)

and (2)



(80)

Diagram 1 belongs to the prototype

(81)

which is easily included, and in the scheme of Meeron is even included in the simplest $\psi$-bond prototype

(82)

whereas diagram 2, which has only two more $g$-bonds, belongs to the prototype

(83)

which is not likely to be investigated at all. It might be that this is as it should be, but there is no proof that such is the case, nor is there an apparent way at present to analyze the problem.

However, in spite of such limitations, the rise of cluster techniques in the past decade involving selective resummations constitutes a considerable advance, since previously no way was available to obtain finite approximations.

The value of this study should be discussed. The development based on ALSC and LTSC diagrams leading to equation 62 is an original contribution, the exact worth of which is yet unclear. The development leading to equation 70 is essentially equivalent to a previous development of the radial distribution function (16), but is useful in showing the exact relation between this work and that of Mazo and Zemach (3), which formed the starting point of this study.

It may be in the future that applications will arise for which the irreducible diagram development would be inapplicable or awkward, necessitating the use of the development leading to equation 62. An example of such a possibility might be a method of using reducible classical cluster diagrams to order contributions for a quantum mechanical treatment.

In addition, the extension of Mazo and Zemach's work to the multicomponent case is of interest in itself, as may be the various summations of convolutions leading to equations 53, 54, 55, and 58 through 60.

## APPENDIX 1

## PROOF OF MAYER'S "CHAIN-SHRINKING" THEOREM (5)

Consider an integral, $B_{\underset{\sim}{\ell}}$, with an integrand consisting of a sum of products of $f$ functions corresponding to diagrams on the set of vertices $\underset{\sim}{\ell}$, including a factor $(\underset{\sim}{\ell}!)^{-1}$ in the definition, and consider a series, of which this integral, multiplied by $\underset{\sim}{\varsigma}^{\underset{\sim}{\ell}}$ is a term.

We need the following lemma, which is actually a fairly simple convolution (16b), but which was originally proved by Montroll and Mayer (26) in a complicated fashion using bilinear expansions in a unit cube:

If

$$q_n(r_{ij}) = \iint\cdots\int g(r_{i1})\, g(r_{12}) \cdots g(r_{n-1,n})\, g(r_{nj})\, d^3r_1 \cdots d^3r_n \,, \qquad \text{(A1)}$$

where $g(r)$ is a radially symmetric function of $r$, and if $G(t)$ is the Fourier transform of $g(r)$,

$$G(t) = 4\pi \int_0^\infty g(r)\, \frac{\sin tr}{tr}\, r^2 dr \,, \qquad \text{(A2)}$$

then the transform, $Q_n(t)$, of $q_n(r)$, is given by

$$Q_n(t) = \left[G(t)\right]^{n+1} \,; \qquad \text{(A3)}$$

and if

$$\mathscr{g}(r) = \sum_{n=0}^{\infty} (-\kappa^2)^n \mathscr{g}_n(r) \tag{A4}$$

then the transform, $Q(t)$, of $\mathscr{g}(r)$ is given by

$$Q(t) = \frac{1}{\kappa^2 + [G(t)]^{-1}} \tag{A5}$$

In our case,

$$g(r) = e^{-\alpha r}/4\pi r \quad , \tag{A6}$$

$$G(t) = (\alpha^2 + t^2)^{-1} \quad , \tag{A7}$$

and

$$\mathscr{g}(r) = e^{-\kappa r}/4\pi r \tag{A8}$$

in the limit of $\alpha \to 0$, which limit we now take.

Consider now the contribution of a particular diagram, $\eta$, representing one term in the integrand of $B_\ell$, after expansion of the $f$ functions. This diagram can now have any number of solid lines (including zero) and either one or no broken line, joining any two vertices.

If there are no vertices in the diagram which are connected by being in chains of $g$-bonds, the diagram is called a prototype. Each diagram, $\eta$, "belongs" to a prototype, $\zeta$, obtained by replacing all $\mathscr{g}$-bonds chains by lines. In general, there will be a number, $\nu$, of $g$-bond chains in $\eta$, and we shall call the vertices in the chains the set $\underset{\sim}{n}$. We call further the set in chain number $\alpha$ the set $\underset{\sim}{n}_{\alpha}$. The vertices not in chains will be called the set $\underset{\sim}{m}$.

The integral of the single term corresponding to the diagram $\eta$ is

$$(-\lambda)^{\nu}\left[\prod_{s=1}^{\sigma} z_s^{\nu_s}\right]\left\{\prod_{\alpha=1}^{\nu}\left[\prod_{s=1}^{\sigma}\left(-\lambda z_s^{2}\right)^{n_{\alpha s}}\right]\right\} I_{\underset{\sim}{m}(\zeta)}, \qquad \text{(A9)}$$

where $I_{\underset{\sim}{m}(\zeta)}$ is the integral corresponding to the prototype $\zeta$, except that $g_{n_\alpha}$ replaces the $\alpha^{th}$ bond. The number of chain ends attached to vertices of species $s$ is $\nu_s$. Note that

$$\sum_{s=1}^{\sigma} \nu_s = 2\nu .$$

Expression 9 must be multiplied by $\underset{\sim}{z}^{\underset{\sim}{\ell}}$, by $(\underset{\sim}{\ell}!)^{-1}$, and by the total number of terms leading to identical contributions when we sum over $\eta$. This last combinatorial coefficient is equal to the cominatorial coefficient of the prototype, $A_{\underset{\sim}{m}(\zeta)}$, multiplied by:

1) The number of ways of selecting the sets $\underset{\sim}{m}, \underset{\sim}{n}_1, \cdots \underset{\sim}{n}_\nu$ from $\underset{\sim}{\ell} = \underset{\sim}{m} + \underset{\sim}{n}$, which is:

$$\frac{(\underset{\sim}{m}+\underset{\sim}{n})!}{\underset{\sim}{m}!\prod_{\alpha=1}^{\nu}\underset{\sim}{n}_{\alpha}!} ;$$

and 2) The number of ways of ordering the particles in the chains, which is:

$$\prod_{\alpha=1}^{\nu} n_\alpha !$$

where

$$n_\alpha = \sum_{s=1}^{\sigma} n_{\alpha s} \quad .$$

Collecting the above factors gives

$$(-\lambda)^{\nu}\left[\prod_{s=1}^{\sigma} z_s^{\nu_s}\right]\underset{\sim}{c}^{\underset{\sim}{m}}\frac{A_{\underset{\sim}{m}(\zeta)}}{\underset{\sim}{m}!}\left\{\prod_{\alpha=1}^{\nu} n_\alpha ! \prod_{s=1}^{\sigma}\left[\frac{(-\lambda z_s^2 c_s)^{n_{\alpha s}}}{\prod_{\alpha=1}^{\nu} n_{\alpha s}!}\right]\right\} I_{\underset{\sim}{m}(\zeta)} \,. \qquad \text{(A10)}$$

This now needs to be summed over all possible chain compositions and lengths to give the summed contributions of all diagrams belonging to the prototype $\zeta$ .

First we sum over all possible compositions of the chains for a certain set of chain lengths, $n_1, n_2, \dots, n_\nu$. That is, we sum over all $n_{\alpha s}$ such that $\sum_{s=1}^{\sigma} n_{\alpha s} = n_\alpha$. This affects only the part in curly brackets, which becomes

$$\prod_{\alpha=1}^{\nu} \sum_{\substack{n_{\alpha s} \\ \left(\sum_{s=1}^{\sigma} n_{\alpha s} = n\right)}} n_\alpha ! \prod_{s=1}^{\sigma}\left[\frac{(-\lambda z_s^2 c_s)^{n_{\alpha s}}}{\prod_{\alpha=1}^{\nu} n_{\alpha s}!}\right] \,. \qquad \text{(A11)}$$

However, by the multinomial theorem, this is exactly

$$\prod_{\alpha=1}^{\nu}\left(-\lambda\sum_{s=1}^{\sigma} z_s^{2} c_s\right)^{n_\alpha} \equiv \prod_{\alpha=1}^{\nu}\left(-\kappa^{2}\right)^{n_\alpha}, \qquad \text{(A12)}$$

where $\kappa$ is the Debye inverse shielding length.

Expression A10 now becomes

$$(-\lambda)^{\nu}\left[\prod_{s=1}^{\sigma} z_s^{\nu_s}\right]\underset{\sim}{c}^{\underset{\sim}{m}}\left(\prod_{\alpha=1}^{\nu}\left(-\kappa^{2}\right)^{n_\alpha}\right)\frac{A_{\underset{\sim}{m}}(\zeta)}{\underset{\sim}{m}!}\, I_{\underset{\sim}{m}}(\zeta) \, . \qquad \text{(A13)}$$

Since the integrand of $I_{\underset{\sim}{m}}(\zeta)$ has $q\, n_\alpha$ in it for the bonds $\alpha = 1, 2, \ldots, \nu$, summing over all $n_\alpha$ from $0$ to $\infty$ gives from expression A13 and Mayer's lemma:

$$(-\lambda)^{\nu}\left[\prod_{s=1}^{\sigma} z_s^{\nu_s}\right]\underset{\sim}{c}^{\underset{\sim}{m}}\frac{A_{\underset{\sim}{m}}(\zeta)}{\underset{\sim}{m}!}\, I'_{\underset{\sim}{m}}(\zeta) \, . \qquad \text{(A14)}$$

Here $I'_{\underset{\sim}{m}}(\zeta)$ is the integral corresponding to the prototype $\zeta$ with $q(r)$ replacing all chains in the integrand.

But expression A14 has exactly the form of the contribution of the prototype to the original series $\sum_{\underset{\sim}{l}} B_{\underset{\sim}{l}}\underset{\sim}{c}^{\underset{\sim}{l}}$ except for the fact that bonds have been replaced by $q$-bonds, so we have reduced the contributions of all diagrams to a sum of the original form, but involving only prototype diagrams having $q$-bonds instead of $g$-bonds. In such prototypes we choose to use "wiggly" lines for the

$\rho$ -bonds, retaining broken lines for the $k$ -bonds, following Salpeter (17).

## APPENDIX 2

## PROOF OF EQUATION 60

We want to show that equation 60 is the correct expression for the coefficients in equation 58.

We assume that equation 60 holds for all values of $p \leq n$, and substitute into the right hand side of equation 58; obtaining:

$$C^{s}_{n+1} = s\sum_{t=1}^{s} \frac{t^{n}(-1)^{t-s}}{t!(s-t)!} + \sum_{t=1}^{s-1} \frac{t^{n}(-1)^{t-s+1}}{t!(s-t-1)!} \tag{A15}$$

$$= s\sum_{t=1}^{s} \frac{t^{n}(-1)^{t-s}}{t!(s-t)!} + \sum_{t=1}^{s-1} \frac{t^{n}(-1)^{t-s+1}(s-t)}{t!(s-t)!} \tag{A16}$$

$$= \sum_{t=1}^{s-1} \frac{t^{n+1}(-1)^{s-t}}{t!(s-t)!} + \frac{s^{n+1}(-1)^{0}}{s!\,0!} \tag{A17}$$

$$= \sum_{t=1}^{s} \frac{t^{(n+1)}(-1)^{t-s}}{t!(s-t)!} \;. \tag{60}$$

Thus equation 60 is established for the case $s < p$. The case $s = p$ remains, since we are unable to use the recursion relation, because $C_{p-1}^{p}$ is not defined. However, inspection of equation 57 shows that $C_p^p$ must always equal unity, so we need only show that equation 60 gives unity for $s = p$.

We assume $C_r^r = 1$ and show $C_{r+1}^{r+1} = C_r^r$. From equation 60, we have

$$C_{r+1}^{r+1} - C_r^r = \sum_{t=1}^{r+1} \frac{t^{r+1}(-1)^{t-r-1}}{t!(r-t+1)!} - \sum_{t=1}^{r} \frac{t^r(-1)^{t-r}}{t!(r-t)!} \tag{A18}$$

$$= \sum_{t=1}^{r+1} \frac{t^{r+1}(-1)^{t-r-1}}{t!(r-t+1)!} + \sum_{t=1}^{r} \frac{t^r(-1)^{t-r-1}(r-t+1)}{t!(r-t+1)!} \tag{A19}$$

$$= \sum_{t=1}^{r+1} \frac{t^r(-1)^{t-r-1}(r+1)}{t!(r-t+1)!} \tag{A20}$$

$$= \sum_{s=0}^{r} \frac{(s+1)^{r-1}(-1)^{s-r}(r+1)}{s!(r-s)!} \; . \tag{A21}$$

Now expression A21 is proportional to

$$\sum_{s=0}^{r} \frac{(s+1)^{r-1}(-1)^{r-s}r!}{s!(r-s)!} \; , \tag{A22}$$

which we show is zero. Consider the quantity:

$$x(x-1)^r = \sum_{s=0}^{r} \frac{r!\,(-1)^{r-s}\,x^{s+1}}{s!\,(r-s)!} \tag{A23}$$

We can obtain expression A22 from A23 by the following recipe:

$$\left(x\frac{d}{dx}\right)^{r-1}\left[x(x-1)\right]\Big|_{x=1} = \sum_{s=0}^{r} \frac{r!\,(-1)^{r-s}(s+1)^{r-1}\,x^{s+1}}{s!\,(r-s)!}\Bigg|_{x=1} \tag{A24}$$

$$= \sum_{s=0}^{r} \frac{r!\,(-1)^{r-s}(s+1)^{r-1}}{s!\,(r-s)!} \quad ,$$

which is the same as expression A22.

But if we operate directly on $x(x-1)^r$, $r-1$ or fewer times with $x\,d/dx$, we note immediately that every term in the result must contain $(x-1)$ at least to the first power, causing the result to vanish when $x=1$ is substituted.

Therefore

$$C_{r+1}^{r+1} - C_r^r = 0 \quad , \tag{A25}$$

and equation 60 is established.

# APPENDIX 3

## EXTENSION OF SALPETER'S METHOD (17) TO THE MULTICOMPONENT CASE

For this appendix, we shall consider only the derivation of the activity coefficient expression in terms of a fugacity series.

Equation 26 is

$$w_{0,0,\underset{\sim}{N}-\underset{\sim}{n}} = \underset{\sim}{z}^{\underset{\sim}{n}} w_{0,0,\underset{\sim}{N}} \quad . \tag{26}$$

The integral $w_{0,0,\underset{\sim}{N}}$ is the configuration integral, but Salpeter uses a different definition of the configuration integral, which we adopt for this appendix and extend to the multicomponent case:

$$\begin{aligned} Z_{\underset{\sim}{N}} &\equiv \frac{1}{V^N}\int\cdots\int e^{-\beta U} d^3r_1 \ldots d^3r_{N_\sigma} \\ &= \frac{\underset{\sim}{N}!}{V^N} w_{0,0,\underset{\sim}{N}} \quad . \end{aligned} \tag{A26}$$

Equation 26 becomes, for $n \ll N$:

$$\frac{\underset{\sim}{z}^{\underset{\sim}{n}}}{\underset{\sim}{c}^{\underset{\sim}{n}}} = \gamma^{\underset{\sim}{n}} = \frac{Z_{\underset{\sim}{N}-\underset{\sim}{n}}}{Z_{\underset{\sim}{N}}} \quad . \tag{A27}$$

We now want an expression for

$$\frac{1}{\gamma_i} = Z_{\underset{\sim}{N}} \Big/ Z_{\underset{\sim}{N}-1_i} \tag{A28}$$

Consider $Z_{\underset{\sim}{N}}$. Assume the separability of the potential energy, $U$, in equation A26 into pair forces, and write $e^{-\beta U}$ as a sum of cluster terms, as is usually done. A general term in this expansion is represented by a diagram with the entire set $\underset{\sim}{N}$ as vertices, and an arbitrary set of lines connecting some or all of them in one or more groups. Consider a term with a diagram consisting of one ALSC part containing particle $1_i$ and the set $\underset{\sim}{\ell}$, plus other disconnected parts.

Let

$$I_{(\underset{\sim}{\ell}+1_i)\eta} = \frac{1}{V^{\ell+1}} \int \prod f \, d^3r_i \, d^3r^{(\underset{\sim}{\ell})} \tag{A29}$$

be the integral over the set $\underset{\sim}{\ell}+1_i$ of the product of $f$ functions belonging to the ALSC part. Summing all terms in $Z_{\underset{\sim}{N}}$ with the particular ALSC part and all other disconnected parts must give

$$I_{(\ell+1_i)\eta} \, Z_{\underset{\sim}{N}-\underset{\sim}{\ell}-1_i} \quad . \tag{A30}$$

This we multiply by the number of ways to select the set $\underset{\sim}{\ell}$ from the set $\underset{\sim}{N}-1_i$ :

$$\frac{(\underset{\sim}{N}-1_i)!}{\underset{\sim}{\ell}!\,(\underset{\sim}{N}-\underset{\sim}{\ell}-1_i)!} \quad . \tag{A31}$$

The cluster integral, $b_{\underset{\sim}{n}}$, is defined as usual,

$$b_{\underset{\sim}{\ell}+l_i} \equiv \frac{1}{(\underset{\sim}{\ell}+l_i)!\,V}\int \sum_{\eta} \prod f\, d^3 r^{(\ell+l_i)} = \frac{V^{\ell}}{(\underset{\sim}{\ell}+l_i)!} \sum_{\eta} I_{(\underset{\sim}{\ell}+l_i)\eta}, \qquad \text{(A32)}$$

where $\sum_{\eta}$ means a sum over all ALSC diagrams on the set $\underset{\sim}{\ell}+l_i$.

The total contribution to $Z_{\underset{\sim}{N}}$ from all diagrams in which $l_i$ occurs in a cluster with a set $\underset{\sim}{\ell}$ is then

$$\frac{(\underset{\sim}{N}-l_i)!}{V^{\ell}(\underset{\sim}{N}-\underset{\sim}{\ell}-l_i)!}(l_i+1)\, b_{\underset{\sim}{\ell}+l_i}\, Z_{\underset{\sim}{N}-\ell-l_i} \qquad \text{(A33)}$$

.

Using equation A27 and summing over all sets $\underset{\sim}{\ell}$, we find

$$\frac{1}{\gamma_i} = \sum_{\underset{\sim}{\ell}=0}^{\underset{\sim}{N}-l_i} (l_i+1)\, b_{\underset{\sim}{\ell}+l_i}\, \underset{\sim}{z}^{\underset{\sim}{\ell}} \qquad \text{(A34)}$$

.

This is the desired result. Extensions of other expressions of Salpeter are similar.

# GLOSSARY OF SYMBOLS

| | |
|---|---|
| $a_i(\rho_{\alpha_i})$ | Parametric function in generating functionals |
| $a_{ij}$ | Distance of closest approach of ions of type $i$ and $j$ |
| $A$ | Helmholtz free energy |
| $A_{\underset{\sim}{m}}(\zeta)$ | Combinatorial coefficient |
| $b_{\underset{\sim}{n}}$ | Mayer's reducible cluster integral |
| $b_i(\sigma_{\alpha_i})$ | Parametric function similar to $a_i(\rho_{\alpha_i})$ |
| $B_{\underset{\sim}{n}}$ | Mayer's irreducible cluster integral |
| $c_i$ | Concentration of component $i$ in particles/unit volume |
| $c_i(\xi_{\alpha_i})$ | Parametric function similar to $a_i(\rho_{\alpha_i})$ |
| $C_p^s$ | Coefficient of $(-\kappa r)^s$ in $P_p$ |
| $D$ | Dielectric constant |
| $\epsilon$ | Magnitude of the electron charge |
| $f_{ij}$ | Mayer's cluster expansion function |
| $f^{(\underset{\sim}{N})}$ | Distribution function of $\underset{\sim}{N}$ particles in phase space |
| $f^{(\underset{\sim}{n})}$ | Reduced distribution function depending on $\underset{\sim}{n}$ coordinates and $\underset{\sim}{n}$ momenta |
| $f^{(\underset{\sim}{n},\underset{\sim}{m})}$ | Reduced distribution function depending on $\underset{\sim}{n}$ coordinates and $\underset{\sim}{m}$ momenta |
| $F_{ij}$ | Function in equation 72 |
| $g_{ij}^{(2)}(r_{1_i 1_j})$ | Two-body correlation function or radial distribution function |
| $g_{ij}(r_{1_i 1_j})$ | Function in equation 44 |
| $G(t)$ | Fourier transform of $g_{ij}(r)$ |

| | |
|---|---|
| $G_U$ | Generating functional for $U$ functions |
| $G_W$ | Generating functional for $W$ functions |
| $H$ | System hamiltonian |
| $I^{ij}_{\underset{\sim}{\ell}}$ | Cluster integral (see equation 42) |
| $I^{ij}_{\underset{\sim}{\ell}(\eta)}$ | Contribution to $I^{ij}_{\underset{\sim}{\ell}}$ from diagram $\eta$ |
| ${}^{o}I^{ij}_{\underset{\sim}{m}(\zeta)}$ | Zero order contribution of prototype $\zeta$ to equation 62 |
| ${}^{p}_{\{p_\alpha\}}I^{ij}_{\underset{\sim}{m}(\zeta)}$ | $p^{th}$ order contribution of prototype to equation 62 |
| $I_{\underset{\sim}{m}(\zeta)}$ | Integral in equation A9 |
| $I'_{\underset{\sim}{m}(\zeta)}$ | Integral in equation A14 |
| $\mathcal{J}^{ij}_{\underset{\sim}{k}}$ | Cluster integral in equation 69 |
| $\mathcal{J}^{ij}_{\underset{\sim}{k}(\xi)}$ | Contribution to $\mathcal{J}^{ij}_{\underset{\sim}{k}}$ from diagram $\xi$ |
| ${}^{o}\mathcal{J}^{ij}_{\underset{\sim}{k}}$ | Prototype cluster integral in equation 70 |
| $k$ | Boltzmann's constant |
| $k_{ij}(r_{l_i l_j})$ | Function in equation 44 |
| $\ell^*$ | The set $\underset{\sim}{\ell} = (\ell_1, \ell_2, \ldots, \ell_\sigma)$ plus particles $l_i$ and $l_j$ |
| $\underset{\sim}{m}^*$ | The set in the prototype part of a diagram in "chain-shrinking" proof |
| $\underset{\sim}{n}$ | The set in the chains of a diagram |
| $n$ | Total number of particles in set $\underset{\sim}{n}$ |
| $\underset{\sim}{n}_\alpha$ | Set of particles in chain $\alpha$ |
| $\underset{\sim}{N}$ | Set of all charged particles |
| $p_i$ | Momentum of particle $i$ |
| $P_p$ | Polynomial in $g^{(p)}(r)$ |
| $g^{(p)}(r)$ | General chain-replacing function |
| $g_n(r)$ | Function in Appendix 1 (see equation A1) |

| | |
|---|---|
| $Q_n(t)$ | Fourier transform of $g_n(r)$ |
| $Q_{\underline{N}}$ | Partition function |
| $r_{\alpha_i}, R_{\alpha_i}$ | Coordinates of particle $\alpha_i$ |
| $r_{l_i l_j}$ | The scalar separation of particles $l_i$ and $l_j$ |
| $S_i$ | Sum in Mayer expression for fugacity |
| $T$ | Temperature |
| $u_{\underline{m},\underline{n},\underline{k}}$ | General cluster integral |
| $u'_{l_i,l_j,\underline{k}}$ | Special cluster integral (see equation 41) |
| $U_{\underline{N}}$ | Cluster functions |
| $U_{\underline{M},\underline{N},\underline{K}}$ | General cluster functions |
| $V$ | Volume of system |
| $w_{\underline{m},\underline{n},\underline{k}}$ | General separable function integrals |
| $w^{*}_{ij}$ | Short-range repulsive potential |
| $W_{\underline{N}}$ | Distribution function in Mazo-Zemach formalism |
| $W_{\underline{M},\underline{N},\underline{K}}$ | General separable function |
| $W^{(n)}$ | Potential of mean force |
| $Z_i$ | Charge number of ion of type |
| $z_i$ | Fugacity of component |
| $Z_{\underline{N}}$ | Configuration integral in Appendix 3 |
| $\beta$ | $\equiv (kT)^{-1}$ |
| $\gamma_i$ | Activity coefficient of component $i$ $(\equiv z_i/c_i)$ |
| $\Gamma_s$ | Function in equation 75 (see equation 76) |
| $\Gamma_{st,1}$ | Function in equation 75 (see equation 77) |
| $\Gamma_{st,2}$ | Function in equation 75 (see equation 78) |
| $\delta_{ij}$ | Kronecker delta |

| | |
|---|---|
| $\delta(r)$ | Dirac delta function |
| $\kappa$ | Debye inverse length (see equation 8) |
| $\lambda$ | $\equiv 4\pi e^2/DkT$ |
| $\nu$ | Number of chains in a diagram |
| $\varphi_{ij}(r)$ | Potential function |
| $\psi_{ij}(r)$ | Function represented by Meeron's " $\psi$-bond" |

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# III. APPROXIMATIONS TO TIME-DEPENDENT ENSEMBLE AVERAGES

## A. INTRODUCTION

### 1. Explanation of the Problem

In equilibrium statistical thermodynamics, one is generally interested in ensemble averages of various functions which are not explicitly dependent on the time, and which have time-independent ensemble averages. The arguments of these functions are the coordinates and momenta of particles in the system, measured at a single time.

If we, however, desire the ensemble average of a function having as arguments positions and momenta measured at two or more different times, we find this average to depend on the times at which the coordinates and momenta are to be measured, even in an equilibrium ensemble.

For example, consider the ensemble average

$$\left\langle \beta(t_0)\,\alpha(t_0+s) \right\rangle = \int f^{(N)}(\mathcal{R}_0,\mathcal{P}_0)\,\beta(\mathcal{R}_0,\mathcal{P}_0)\,\alpha(\mathcal{R},\mathcal{P})\,d\mathcal{R}_0\,d\mathcal{P}_0 \quad , \qquad (1)$$

where $\beta$ and $\alpha$ are arbitrary functions of coordinates and momenta and do not depend explicitly on time. We write $\beta(t_0)$ for $\beta(\mathcal{R}[t_0],\mathcal{P}[t_0])$ and $\alpha(t_0+s)$ for $\alpha(\mathcal{R}(t_0+s),\mathcal{P}(t_0+s))$ . where the time arguments of the coordinates and momenta indicate the times at which they are to be measured, and $\mathcal{R}$ and $\mathcal{P}$ represent the coordinates and momenta of all particles in the system. We will usually employ the shorthand notation,

$$\mathcal{R}_0 = \mathcal{R}(t_0) \quad , \quad \mathcal{P}_0 = \mathcal{P}(t_0)$$
$$\mathcal{R} = \mathcal{R}(t) \quad , \quad \mathcal{P} = \mathcal{P}(t)$$

where $t = t_0 + s$ . In equation 1, $f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; t_0)$ is the distribution function of the entire system.

Since the classical systems in our ensemble are governed by deterministic equations of motion,

$$\mathcal{R} = \mathcal{R}(\mathcal{R}_0, \mathcal{P}_0, s) \quad ; \quad \mathcal{P} = \mathcal{P}(\mathcal{P}_0, \mathcal{R}_0, s) \ . \tag{2}$$

The ensemble average in equation 1 is a function of $s$ (as well as being a functional of $f^{(N)}$, $\beta$, and $\alpha$ ), even in an equilibrium ensemble.

In the case that $\beta$ and $\alpha$ are the same functional form, expression 1 is called an autocorrelation function, or loosely, a time-correlation function, and may be of considerable interest. If the functions are complex, the complex conjugate of $\alpha$ is used in equation 1. Such functions are of interest in the Kirkwood theory of Brownian motion (1), and in the theory of nuclear spin relaxation (2).

Time-correlation functions and other functions of the type of equation 1 can be defined for equilibrium and for non-equilibrium systems, if we assume these to be representable by a Gibbsian ensemble (3). In this case, $f^{(N)}$ depends explicitly on $t$.

In addition to studying ensemble averages of the form of equation 1, non-equilibrium statistical mechanics concerns itself directly with the related study of the time evolution of $f^{(N)}$ and its reduced distribution functions, $f^{(n)}$, which are also explicitly time-dependent.

In this study, we shall consider first the evolution of ion distribution functions in a non-equilibrium electrolytic solution, and shall then consider time-dependent ensemble averages in ionic solutions and gases of charged particles.

## 2. Survey of the Literature

There is a considerable body of literature concerning the evolution of distribution functions in non-equilibrium ensembles, and this survey will not attempt to be exhaustive, or even completely representative. In addition to this survey, some references will be introduced in the development to follow.

In 1946, Kirkwood (1) began a long series of papers on irreversible statistical mechanics by deriving a differential equation governing the evolution of a one-particle distribution function under assumptions appearing reasonable for a heavy particle immersed in a fluid of lighter particles, but perhaps also giving a reasonable approximation for other cases. This equation is of the form of the Fokker-Planck equation in phase space (4). Kirkwood's derivation was later refined by Ross (5), and Helfand (6) studied the friction constant in the equation under a linear trajectory approximation. Brittin (7) has extended the original Kirkwood formalism to apply specifically to a fully ionized gas.

Rice and his collaborators (8) have begun an investigation of moderately dense fluids, beginning where the original Kirkwood articles ended (9), with rigid spheres. After considering rigid spheres, they worked with rigid spheres having weak attractive potentials, and essentially combined the hard-sphere and Brownian motion treatments.

There are many other treatments of the time evolution of distribution functions, including the elegant methods of Prigogine (10a) which are not understood by the present author. Weinstock (10b) has published an expansion of the Green's function solution of Liouville's equation for a system of hard spheres, giving the time evolution of the distribution function, and Andrews (11) has also treated this evolution in dense fluids.

Further survey of work on fluids in general will not be attempted, but some relevant references from work on plasmas and electron gases will be cited. No references were found to work on the evolution of distribution functions in ionic solutions, but there are many articles which deal with plasmas. Thompson's review of plasma dynamics covers up to about the end of 1959 (12), and may be consulted for references. Since then, many articles have been written. One of the most widely-quoted is that of Rostoker and Rosenbluth (13). They treat a plasma in which one particle is singled out as a test particle, and by expanding the hierarchy of equations obtained by integration of the Liouville equations, obtain an equation governing the time evolution of reduced distribution functions.

There are extensions and refinements of the work of Rostoker and Rosenbluth (14) and there are several other treatments, for example references (15) to (18). In most treatments, only the coulomb part of the potential is retained, and close approaches are usually neglected.

Ron and Kalman (19a, 19b, 19c) have also studied the interaction of a test particle with a plasma, using an approach based on the Fokker-Planck equation approach of Gasiorowicz, Neuman, and Riddell (19d), which is based on the original approach of Kirkwood (1).

Von Roos has solved the Vlasov equation (20a), using a diagram technique which he developed for the solution of the Liouville equation (20b), and which is of more general interest. Any other articles of interest to us will be mentioned in the development to follow.

It does not appear that there are many articles in the literature especially concerned with classical time correlation functions. However, Oppenheim and Bloom (2) apply them to nuclear spin relaxation and derive some approximate expressions for time-displaced reduced distribution functions, which can be used to obtain such averages. Vineyard (21) also presents some formal results with such distribution functions. Taylor (22) has obtained the time correlation function of the electric field in a plasma, to a zeroth approximation, and has used it to express the dynamical friction on a test particle.

## B. APPROACHES TO THE TIME EVOLUTION PROBLEM

In any dynamical system, the behavior in time of any function, $\varphi$ , of coordinates and momenta of particles in the system is given by

$$\frac{d\varphi}{dt} = \frac{\partial\varphi}{\partial t} + [H, \varphi] , \tag{3}$$

where $d\varphi/dt$ is the time derivative of the arbitrary function $\varphi$ taken along the natural trajectory in the 6-N-dimensional phase space, $\partial\varphi/\partial t$ is the partial derivative of the functional form with all the generalized coordinates, $q_i$ , and all the generalized momenta, $p_i$ , fixed, and

$$[H, \varphi] = \sum_i \left( \frac{\partial\varphi}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\varphi}{\partial p_i}\frac{\partial H}{\partial q_i} \right) \tag{4}$$

is the Poisson bracket of $H$ (the Hamiltonian of the complete system) and $\varphi$ .

Liouville's theorem (23) states that if $\varphi$ is the phase space density function, $f^{(N)}$, then expression 3 vanishes, so that

$$\frac{\partial f^{(N)}}{\partial t} = -[H, f^{(N)}] \equiv i L f^{(N)} . \tag{5}$$

The second equality defines the hermitian Liouville operator, $\mathcal{L}$ . Equation 5 is the starting point of most time-dependent problems in statistical mechanics, but it is also possible to try to work with the equations of motion of the individual particles. This is what Pines and Bohm (24) did in their collective coordinate treatment of a classical plasma, represented by a one-component charged gas neutralized by a uniform background. Their success suggests a trial of collective coordinates for ionic solutions, in an attempt to avoid treating the solvent as a molecular fluid.

If we begin by taking an electrically neutral, multi-component gas of particles interacting only through Coulomb force, we can go through the Pines-Bohm random-phase approximation procedure, and obtain the result that collective oscillations occur. Presumably, all of their work with dispersion relations, etc., could be so extended.

Next, we can try representing the solvent as a structureless fluid with a dielectric constant, through which the ions move, experiencing a viscous drag. In this system, we might hope to find suitable collective coordinates that will show damped oscillations. Attempts were made to find such coordinates, but the presence of the friction terms made the problem intractable.

Even if this had been successful, we would have been left with an unphysical asymptotic picture of motionless ions. A stochastic term could have been added, but although there are mechanisms to excite collective oscillations in plasmas, to assume such in an ionic solution would be unwarranted, since the bombardment of individual ions in a solution by solute molecules is certainly not collective, or even collectively stochastic.

If we abandon attempts to work with collective coordinates, there is still another possibility to try before we give up trying to ignore the molecular nature of the solvent. It is known (25) that non-conservative systems can be treated with Lagrangian methods if the dissipative forces are proportional to the velocity of the particles on which they act. If we assume this for our ions in their solvent, we can derive a modified Liouville equation for the distribution function of the ions.

If we use the dissipation function of Rayleigh,

$$\mathcal{F} = \frac{1}{2} \sum_{i=1}^{N} k_i \left( V_{ix}^2 + V_{iy}^2 + V_{iz}^2 \right) \quad , \qquad (6)$$

where $k_i$ is the friction constant of particle $i$ , such that the frictional force is

$$\vec{F}_{fi} = -k_i \vec{V}_i$$

and the $V$'s are velocity components, then Lagrange's equations become (25):

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial q_i} + \frac{\partial \mathcal{F}}{\partial \dot{q}_i} = 0 . \qquad (7)$$

Using equation 7 instead of the ordinary Lagrange's equations in deriving Liouville's theorem gives, for cartesian coordinates:

$$\frac{\partial f}{\partial t} + \sum_i \left(\frac{\partial f}{\partial p_i}\dot{p}_i + \frac{\partial f}{\partial q_i}\dot{q}_i\right) = f \sum_i \frac{\partial^2 \mathcal{F}}{\partial p_i \partial \dot{q}_i} = kf , \qquad (8)$$

where $k = \sum_i \frac{k_i}{m_i}$ .

It can be shown that density functions satisfying equation 8 retain their normalization for all time, but if we write 8 as

$$i \frac{\partial f}{\partial t} + L' f = 0 , \qquad (9)$$

then $L'$ is not hermitian. This is not a serious drawback unless we were to try elegant techniques such as Prigogine's or Andrews', which require real eigenvalues for $L$ .

More serious is the fact that we could not include stochastic terms in the Lagrangian equations, since these are neither derivable from a potential nor proportional to a velocity, resulting again in the unphysical motionless state as $t \rightarrow \infty$.

We conclude that there is nothing to be gained by ignoring the molecular nature of the solvent, and turn our attention to the entire system of particles.

The dynamical behavior of the system is governed by Liouville's equation, equation 5, which describes the time evolution of the phase density, or distribution function, for all $N$ particles. This equation is valid whether the ensemble represents an equilibrium or a nonequilibrium system.

Beginning with equation 5 and integrating over the coordinates and momenta of all of the particles except one, it is possible to obtain an equation of the Fokker-Planck type in the phase space of one particle (1, 5). The result of Ross is (5):

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\vec{P}_1}{m} \cdot \nabla_{r_1} \bar{f}^{(1)} + \nabla_p \cdot \left(\vec{F}_1^{\,*} + \vec{X}_1\right) \bar{f}^{(1)} = \nabla_{p_1} \cdot \zeta_1 \left\{ \frac{\vec{P}_1}{m_1} \bar{f}^{(1)} + kT \nabla_{p_1} \bar{f}^{(1)} \right\}, \qquad (10)$$

where the friction constant, $\zeta_1$, is defined:

$$\zeta_1 = \frac{N_2}{3kT\tau} \int_0^{\tau} \int_{-s}^{0} \int \cdots \int \vec{F}_{12}(r_{12}) \vec{F}_1\left(R + [s+s'] \frac{P}{m}\right) {}^{\circ}f^{(1/N)}(r_1, p_1 | RP) \qquad (11)$$

$$\times \, dP \, dR \, ds \, ds'$$

and where the other symbols are the same as those of reference (1):

$$\vec{F}^{*} = {}^{1}\langle \vec{F}_1 \rangle^{\circ} + \sum_{\ell=1}^{\sigma} N_\ell \vec{v}_\ell^{\,*} \zeta_\ell' + \vec{F}_1^{\,+} \tag{12}$$

Here ${}^{1}\langle \vec{F}_1 \rangle^{\circ}$ is the equilibrium ensemble mean force on particle 1 with the position and momentum of this particle fixed. The quantity $\vec{F}_1^{\,+}$ is a correction term presumed small and not further evaluated. Also

$$v_\ell^{*} = \frac{N_\ell}{c_\ell} \int \frac{\vec{p}_\ell}{m_\ell} \chi_{1\ell} f_\ell^{(1)}(p_\ell, r_\ell; t)\, dr_\ell\, dp_\ell \quad , \tag{13}$$

where

$$\chi_{1\ell} = \frac{\exp\left(-\beta W_{1\ell}^{(2)}\right)}{6kT \zeta_\ell'} \int_{-\tau_1}^{\tau_1} {}^{1\ell}\langle \vec{F}_{\ell_1} \cdot \vec{F}_\ell \left(R + \frac{sP}{m}\right) \rangle^{\circ} ds. \tag{14}$$

Here $W_{1\ell}^{(2)}$ is the equilibrium potential of mean force between particles 1 and $\ell$, and $\tau_1$, is a time large enough to allow the integral to attain a "plateau value" which Kirkwood assumes to exist. Note that the equation involves the time-smoothed distribution function

$$\bar{f}^{(1)}(r_1, p_1, t) \equiv \frac{1}{\tau} \int_0^{\tau} f^{(1)}(r_1, p_1; t+s)\, ds \ . \tag{15}$$

This time-smoothing appears necessary to introduce irreversibility into the dynamics of the system, governed by the time-symmetrical Liouville equation.

In contrast to some of the results of equilibrium statistical mechanics, there is nothing in the derivation of equation 10 that requires the potentials involved to have a finite range, and Gelfand has used equation 11 to calculate a friction constant for a plasma (6). However, the derivations of both Ross and Kirkwood are sufficiently clouded by approximations that it is difficult to tell whether equation 11, which corresponds to the zero-order term of an autocorrelation function (the effects of intermolecular forces are neglected), is a proper approximation to the friction constant. Kirkwood's original expression for $\zeta_1$ is:

$$\zeta_1 = \frac{1}{6kT}\int_{-\tau_1}^{\tau_1} \langle \vec{F}_1(t_0)\vec{F}_1(t_0+s)\rangle^{\circ} ds \quad , \tag{16}$$

which uses the entire autocorrelation function of which equation 11 uses only the zero-order term. In the case of impulsive potentials (such as hard spheres), for example, the linear trajectory approximation may tell very little about actual particle trajectories, and it would seem more sensible to use equation 16 rather than equation 11. However, in the case of impulsive potentials, the entire derivation is not valid, and the Fokker-Planck equation approach becomes questionable.

Rice and Allnatt (8b, 8c) treat systems having hard-core repulsive potentials and soft attractive potentials. Their method essentially separates the effects of the two parts of the potential. The hard-core part of the potential gives rise to a "collision" integral of the same type as that of Rice et al. (9), while the soft part of the potential gives rise to Fokker-Planck terms similar to those in equation 10. The result is

$$D\bar{f}^{(1)} = J_1 + J_2 + \zeta a \bar{f}^{(1)} \tag{17}$$

where

$$D\bar{f}^{(1)} \equiv \frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\vec{p}_1}{m}\cdot\nabla_{r_1}\bar{f}^{(1)} + \nabla_{p_1}\cdot\vec{F}_1^{*}\bar{f}^{(1)}, \tag{18}$$

and

$$a\bar{f}^{(1)} \equiv \nabla_{p_1}\cdot\left\{\left[\frac{\vec{p}_1}{m} - \vec{u}\right]\bar{f}^{(1)} + kT\nabla_{p_1}\bar{f}^{(1)}\right\}. \tag{19}$$

Here $\vec{u}$ is the macroscopic local velocity of the fluid. The friction coefficient, $\zeta$, is the same as in equation 11, except that only the soft part of the potential is included. The "collision" integrals, $J_1$ and $J_2$ are given by

$$\begin{aligned} J_1 = g_0^{(2)}(r_1,\sigma)\iiint\Big[&\bar{f}^{(1)}(r_1,p_1-\Delta p_1;t)\,\bar{f}^{(1)}(r_1,p_2-\Delta p_2;t) \\ &- \bar{f}^{(1)}(r_1,p_1;t)\,\bar{f}^{(1)}(r_1,p_2;t)\Big]\frac{\vec{p}_{12}}{\mu}\,b\,db\,d\epsilon\,dp_2 \end{aligned} \tag{20}$$

$$\begin{aligned} J_2 = g_0^{(2)}(r_1,\sigma)\iiint\Big[&\bar{f}^{(1)}(r_1,p_1-\Delta p_1;t)\,\sigma\vec{k}\cdot\nabla_{r_1}\bar{f}^{(1)}(r_1,p_2-\Delta p_2;t) \\ &+ \bar{f}^{(1)}(r_1,p_1;t)\,\sigma\vec{k}\cdot\nabla_{r_1}\bar{f}^{(1)}(r_1,p_2;t)\Big]\frac{\vec{p}_{12}}{\mu}\,b\,db\,d\epsilon\,dp_2\,, \end{aligned} \tag{21}$$

where $\sigma$ is the hard-core diameter, $\mu$ is the reduced mass, $b$ is the impact parameter, $\epsilon$ is an azimuthal angle, $\vec{k}$ is a unit vector along the line of centers at impact, and $\vec{p}_{12}$ is the relative momentum.

Rice and Allnatt have also solved equation 17 by a Chapman-Enskog procedure, and obtained a result requiring only $\zeta$ and $g_0^{(2)}(\sigma)$ for its evaluation.* A similar solution for equation 11 was derived by Lebowitz, Frisch, and Helfand (26).

As in the case of Kirkwood's Fokker-Planck equation, there is nothing in the derivation of equation 17 requiring the forces to be of short range, so that the problem of the time evolution of one-body distribution functions in an ionic solution is as well in hand as that of ordinary fluids if the friction constant $\zeta$ can be evaluated. Of course, we have the additional complication in computing $\zeta$ that more than one kind of potential occurs, as the solvent-solvent and solvent ion interactions are of short range while the ion-ion interactions are of long range. It would, at first glance, appear that we were faced in this Fokker-Planck equation approach with a task akin to raising ourselves by our bootstraps. We obtain information about the distribution function through an autocorrelation function, but for this we require the distribution function. However, in a linearized theory such as the Fokker-Planck approach of Kirkwood, the zero-order or equilibrium distribution function would seem to suffice for the evaluation of the

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* See equation 29' of reference 8b.

force autocorrelation, and thus in a second-order theory the first-order distribution should suffice for whatever averages must be taken, and so forth.

We now turn our attention to means of obtaining approximations to autocorrelation functions and similar time-dependent ensemble mean values.

## C. TIME-DEPENDENT ENSEMBLE AVERAGES

### 1. Theory

We shall consider the calculation of ensemble averages such as that of equation 1. We use again the notation $\mathcal{R}, \mathcal{P}$ for the coordinates and momenta of all $N$ particles; $r, p$ for the coordinates and momenta of $n$ particles; and $R, P$ for the coordinates and momenta of $N-n$ particles. We also use $t = t_0 + s$, but will later sometimes set $t_0 = 0$.

Since the classical systems in our ensemble are governed by deterministic equations of motion,

$$\mathcal{R} = \mathcal{R}(t) = \mathcal{R}(\mathcal{R}_0, \mathcal{P}_0, s) \tag{22}$$

$$\mathcal{P} = \mathcal{P}(t) = \mathcal{P}(\mathcal{R}_0, \mathcal{P}_0, s) \tag{23}$$

In addition, of course, $\mathcal{R}$ and $\mathcal{P}$ are functionals of the functional form of the equations of motion.

Equation 3 becomes, using the definition of $\mathcal{L}$ (equation 5):

$$\frac{d\alpha}{dt} = -i\mathcal{L}\alpha \tag{24}$$

since $\partial\alpha/\partial t = 0$ by assumption. A formal solution of equation 24 is:

$$\alpha(\mathcal{R},\mathcal{P}) = exp\{-isL\}\,\alpha(\mathcal{R}_0,\mathcal{P}_0) \; . \tag{25}$$

We can now write equation 1:

$$\langle\beta(t_0)\alpha(t_0+s)\rangle = \int f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;t_0)\,\beta(\mathcal{R}_0,\mathcal{P}_0)\,e^{-isL}\,\alpha(\mathcal{R}_0,\mathcal{P}_0)\,d\mathcal{R}_0\,d\mathcal{P}_0 \, . \tag{26}$$

The ensemble average is now explicitly a function of $S$, and we note that the integrand of the right hand side of equation 26 is explicitly a function of "zeroed" variables only.

The theory of the exponential Liouville operator, $exp(-isL)$, has been the subject of considerable research.* However, the work of Prigogine and others in his school is very abstract, involving sophisticated mathematical and diagram techniques, and seems to be of a nature not well suited to use in equation 26. All previous work with the exponential Liouville operator seems to be directed towards the time evolution of distribution functions directly, through the Liouville equation, equation 5, which has the solution:

$$f^{(N)}(\mathcal{R},\mathcal{P},t) = f^{(N)}(\mathcal{R}_0,\mathcal{P}_0,t_0) \tag{27}$$

or

$$f^{(N)}(\mathcal{R}_0,\mathcal{P}_0,t) = exp(isL)\,f^{(N)}(\mathcal{R}_0,\mathcal{P}_0,t_0) \, . \tag{28}$$

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* See, for example, references 1, 10, and 11.

If we were interested only in the time evolution of the distribution function, it would probably be wise to work directly with equation 28, but there are time-correlation functions, such as the one-particle momentum time-correlation function, that are of interest in their own right, so we begin with equation 25.

It is interesting to note that knowledge of the time-dependent distribution function at time $t$ is not enough to calculate a time-correlation function if we do not use the exponential Liouville operator. Distribution functions involving two times are necessary, such as those of Vineyard (21). An alternative formalism can be developed using such functions (see proposition III).

We now return to an approximation scheme using the exponential Liouville operator. By the use of Hamilton's equations and $\vec{F} = \dot{\vec{p}}_i$ , we obtain

$$L = i \sum_{j=1}^{N} \left( \frac{\vec{p}_j}{m_j} \cdot \nabla_{r_j} + \vec{F}_j \cdot \nabla_{p_j} \right) , \qquad (29)$$

where $\vec{F}_j = -\nabla_{r_j} U(\mathcal{R})$ is the force on particle $j$ , and $m_j$ is its mass. At this point, we restrict ourselves to cases in which the kinetic energy is much greater than the potential energy, so that the second term under the sum in equation 29 has much less effect than the first in determining trajectories of particles over short periods of time. Unfortunately, this case is not likely to apply to ionic solutions, so we defer treatment of these until later.

We write

$$L = L^{o} + L^{i} \tag{30}$$

where

$$L^{o} \equiv i \sum_{j=1}^{N} \frac{\vec{P}_j}{m_j} \cdot \nabla_{r_j} \tag{31}$$

and

$$L^{i} \equiv i \sum_{j=1}^{N} \vec{F}_j \cdot \nabla_{P_j} \quad . \tag{32}$$

Thus,

$$\Omega(t,t_o) \equiv e^{-isL} = e^{-is(L^{o}+L^{i})} \quad . \tag{33}$$

This exponential expression can be written using Feynman's operator calculus (28), in which time becomes an operator ordering parameter:

$$\Omega(t,t_o) = exp\left\{-i\int_{t_o}^{t} L^{o}(t')\,dt'\right\} exp\left\{-i\int_{t_o}^{t} L^{i}(t'')\,dt''\right\} . \tag{34}$$

The arguments of the operators do not show any explicit time dependence, but are simply labels interpreted such that

$$L^{o}(t')\,L^{i}(t'')$$

means

$$L^{o}L^{i} \qquad if \qquad t''<t'$$

and

$$L^{i}L^{o} \qquad if \qquad t'<t'' \quad .$$

We expand the second exponential factor, remembering that the presence of the order parameters takes care of all commutation difficulties. (If $L^{\circ}$ and $L^{i}$ were commuting operators, the problem would be much simpler.) Equation 34 becomes

$$\Omega(t,t_0) = \exp\left\{-i\int_{t_0}^{t} L^{\circ}(t')dt'\right\}\left[1 + \sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\left(\int_{t_0}^{t} L^{i}(t'')dt''\right)^n\right]. \qquad (35)$$

The first, or zero-order, term on the right-hand side of equation 35 is the only one that would occur if there were no forces between the particles, and use of it alone results in the linear trajectory approximation (6), in which

$$\begin{aligned} \vec{p}_i(t) &= \vec{p}_i(t_0) \\ \vec{r}_i(t) &= \vec{r}_i(t_0) + s\,\frac{\vec{p}_i}{m_i} \end{aligned} \qquad (36)$$

We now proceed to disentangle the operators in equation 35, writing each term so that the operators act from right to left in the usual manner.

The first-order term becomes

$$\Omega^{(1)}(t,t_0) = -i\int_{t_0}^{t}\Omega^{(0)}(t,t_1)L^{i}(t_1)\Omega^{(0)}(t_1,t_0)dt_1 , \qquad (37)$$

where we write

$$\Omega^{(0)}(t_i,t_j) = \exp\left\{-i\int_{t_j}^{t_i} L^{\circ}(t')dt'\right\} = \exp\left\{-i(t_i-t_j)L^{\circ}\right\}. \qquad (38)$$

The second-order term is

$$\Omega^{(2)}(t,t_0)=\frac{1}{2!}\exp\left\{-i\int_{t_0}^{t}L^{\circ}(t')dt'\right\}\left[(-i)^2\int_{t_0}^{t}\int_{t_0}^{t}L^{i}(t_1)L^{i}(t_2)dt_1dt_2\right]. \tag{39}$$

When this is disentangled, we must have two terms, corresponding to the two possibilities, $t_1 < t_2$ and $t_2 < t_1$. We introduce a step function, $S$:

$$S(x) = \begin{cases} 1 & , x > 0 \\ 0 & , x < 0 \end{cases} . \tag{40}$$

Equation 39 now becomes

$$\Omega^{(2)}(t,t_0)=\frac{1}{2!}\exp\left[-i\int_{t_0}^{t}L^{\circ}(t')dt'\right]\left[-\int_{t_0}^{t}\int_{t_0}^{t}L^{i}(t_1)L^{i}(t_2)S(t_2-t_1)dt_1dt_2\right]$$

$$+\frac{1}{2!}\exp\left[-i\int_{t_0}^{t}L^{\circ}(t')dt'\right]\left[-\int_{t_0}^{t}\int_{t_0}^{t}L^{i}(t_1)L^{i}(t_2)S(t_1-t_2)dt_1dt_2\right]. \tag{41}$$

This expression can be disentangled to yield the following:

$$\Omega^{(2)}(t,t_0)=-\frac{1}{2!}\int_{t_0}^{t}\int_{t_0}^{t}\Omega^{(0)}(t,t_2)L^{i}(t_2)\Omega^{(0)}(t_2,t_1)L^{i}(t_1)\Omega^{(0)}(t_1,t_0)S(t_2-t_1)dt_1dt_2$$

$$-\frac{1}{2!}\int_{t_0}^{t}\int_{t_0}^{t}\Omega^{(0)}(t,t_1)L^{i}(t_1)\Omega^{(0)}(t_1,t_2)L^{i}(t_2)\Omega^{(0)}(t_2,t_0)S(t_1-t_2)dt_1dt_2. \tag{42}$$

Since there is no reason to require a particular order of integration, the two terms in equation 42 differ only in a permutation of integration variables, and so are identical.

We write

$$\Omega^{(2)}(t,t_0) = -\int_{t_0}^{t}\int_{t_0}^{t_1} \Omega^{(0)}(t,t_1) L^{i}(t_1) \Omega^{(0)}(t_1,t_2) L^{i}(t_2) \Omega^{(0)}(t_2,t_0)\, dt_2\, dt_1 , \quad (43)$$

where we change the limits of integration instead of using the step function.

As we continue with the higher-order terms in equation 35, the same pattern occurs. In the nth order term, $n!$ terms occur, differing only in permutations of integration variables, giving

$$\Omega^{(n)}(t,t_0) = (-i)^{n} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n\, \Omega^{(0)}(t,t_1) L^{i}(t_1) \cdots L^{i}(t_n) \Omega^{0}(t_n,t_0) \quad (44)$$

Weinstock (10b) has presented, without derivation, an expression for the Green's function for the Liouville equation which is equivalent to equation 44. However, equation 44 was derived independently, and it appears worthwhile to include this simple derivation. The application of Weinstock is to systems of hard spheres, and is thus more or less unrelated to the present applications.

Equation 44 can be given an interpretation similar to that of Feynman's work in quantum electrodynamics and to diagram techniques in irreversible statistical mechanics: $\Omega^{(0)}(t_i,t_j)$ describes the propagation of the system from time $t_j$ to time $t_i$ as though no forces acted. In equation 44, the right-hand side is interpreted as free propagation from $t_0$ to $t_n$, action of the potential at $t_n$, free propagation from $t_n$ to $t_{n-1}$, etc. The integrations vary the times of each free progation from $0$ to $t-t_0$, keeping their sum equal to $t-t_0$.

Equation 25 now becomes

$$\alpha(\mathcal{R},\mathcal{P})=\Omega(t,t_0)\alpha(\mathcal{R}_0,\mathcal{P}_0)=\sum_{n=0}^{\infty}\Omega^{(n)}(t,t_0)\alpha(\mathcal{R}_0,\mathcal{P}_0). \tag{45}$$

Equation 26 becomes

$$\begin{aligned}\langle\beta(t_0)\alpha(t)\rangle &= \sum_{n=0}^{\infty}\int f^{(N)}(\mathcal{R}_0,\mathcal{P}_0,t_0)\beta(\mathcal{R}_0,\mathcal{P}_0)\Omega^{(n)}(t,t_0)\alpha(\mathcal{R}_0,\mathcal{P}_0)\,d\mathcal{P}_0\,d\mathcal{R}_0 \\ &= \sum_{n=0}^{\infty}\langle\beta(t_0)\alpha(t)\rangle^{(n)}.\end{aligned} \tag{46}$$

In order to use only a few terms of equation 46, we have restricted our discussion to systems in which the potential energy is much smaller than the kinetic energy (with the zero of potential energy taken with all particles infinitely separated). However, if we can devise a way to include large numbers, or perhaps infinite subsets, of terms in equation 46, it can be applied to any system, as no approximations have been used in its derivation. Of course, the implicit assumption of convergence has been made. Further investigation would be necessary to justify this, but we can obtain convergence by avoiding regions of phase space in which $L$ has singularities or other troubles arise. Impulsive potentials might need special attention.

## 2. Calculations

The work of the preceding section will now be applied to the calculation of some approximations to ensemble averages.

### a. Fokker-Planck Friction Coefficient

First we consider, instead of the Fokker-Planck friction coefficient of equation 11 or of equation 16, the averaged coefficient (6):

$$\zeta_{av.} = \frac{\beta}{3\tau}\int_0^{\tau} \langle \vec{F}_1(0)\,\vec{F}_1(t)\rangle\, dt \; . \qquad (47)$$

Helfond (5) calculates $\zeta$ using the linear trajectory approximation, which corresponds to use of only the zero-order term:

$$\zeta_{av.}^{(0)} = \frac{\beta}{3\tau}\int_0^{\tau} \langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(0)} dt \; . \qquad (48)$$

We now calculate the first-order correction to equation 48, which is proportional to

$$\int_0^{\tau} \langle \vec{F}_1(\mathcal{R}_0)\vec{F}_1(\mathcal{R})\rangle^{(1)} dt$$

$$= \int_0^{\tau} dt \int d\mathcal{R}_0\, d\mathcal{P}_0\, f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; 0)\, \vec{F}_1(\mathcal{R}_0) \int_0^{t} dt_1\, \Omega^{(0)}(t, t_1)\, \vec{F}(\mathcal{R}_0)\cdot\nabla_{\mathcal{P}_0}\, \Omega^{(0)}(t, 0)\, F_1(\mathcal{R}_0) \; . \qquad (49)$$

We use a vector notation such that $\vec{F}(\mathcal{R})$, $\mathcal{R}$, $\mathcal{P}$, and $\nabla_{\mathcal{P}_0}$ are vectors with $3N$ components.

In equation 49,

$$\Omega^{(0)}(t_1,0)\vec{F}_1(\mathcal{R}_0) = \vec{F}_1\left(\mathcal{R}_0 + t_1\frac{\mathcal{P}_0}{m}\right) , \qquad (50)$$

where $\mathcal{P}/m$ means $\frac{\hat{e}_{1x}p_{1x}}{m_1} + \frac{\hat{e}_{1y}p_{1y}}{m_1} + \frac{\hat{e}_{1z}p_{1z}}{m_1} + \cdots$ $+ \frac{\hat{e}_{Nx}p_{Nx}}{m_N} + \frac{\hat{e}_{Ny}p_{Ny}}{m_N} + \frac{\hat{e}_{Nz}p_{Nz}}{m_N}$ (the velocity vector $\vec{v}$ in 3N-dimensional space). Inserting equation 50 into equation 49 gives:

$$\int_0^{\tau}\langle\vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)}dt = \int_0^{\tau}dt\int_0^{t}dt_1\int d\mathcal{P}_0 d\mathcal{R}_0 f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;0)$$

$$\Omega^{(0)}(t,t_1)\vec{F}(\mathcal{R}_0)\cdot\nabla_{\mathcal{P}_0}\vec{F}_1\left(\mathcal{R}_0 + t_1\frac{\mathcal{P}_0}{m}\right) . \qquad (51)$$

Since the $\mathcal{P}_0$'s occur only with the $\mathcal{R}_0$'s , we can write instead of $\nabla_{\mathcal{P}_0}$ the operator $t_1\nabla_{\mathcal{R}_0}/m$ , by which we mean

$$t_1\left[\frac{1}{m_1}\left(\hat{e}_{1x}\frac{\partial}{\partial x_{10}} + \hat{e}_{1y}\frac{\partial}{\partial y_{10}} + \hat{e}_{1z}\frac{\partial}{\partial z_{10}}\right) + \cdots\right.$$

$$\left.\cdots + \frac{1}{m_N}\left(\hat{e}_{Nx}\frac{\partial}{\partial x_{N0}} + \hat{e}_{Ny}\frac{\partial}{\partial y_{N0}} + \hat{e}_{Nz}\frac{\partial}{\partial z_{N0}}\right)\right] . \qquad (52)$$

Equation 51 becomes

$$\int_0^{\tau}\langle\vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)}dt = \int_0^{\tau}dt\int_0^{t}dt_1\int d\mathcal{P}_0 d\mathcal{R}_0 f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;0)\times$$

$$\times\vec{F}_1(\mathcal{R}_0)\vec{F}(\mathcal{R}_0+(t-t_1)v_0)\cdot\nabla_{\frac{\mathcal{R}_0+(t-t_1)v_0}{m}}F_1(\mathcal{R}_0+tv_0)\,t_1 . \qquad (53)$$

We write $\vec{F} = -\nabla_R U$, and now consider the case of Helfand, in which $f^{(N)}(\mathcal{R}_0, \mathcal{P}_0, 0)$ can be replaced by the equilibrium distribution function,

$$Q_N^{-1} \exp(-\beta K) \exp(-\beta U(\mathcal{R}_0)) .$$

Now

$$-\left[\nabla_{r_{10}} U(\mathcal{R}_0)\right] e^{-\beta U(\mathcal{R}_0)} = \frac{1}{\beta} \nabla_{r_{10}} \left[e^{-\beta U(\mathcal{R}_0)}\right],$$

so an integration by parts gives

$$\int_0^{\tau} \langle \vec{F}_1(0) \vec{F}_1(t) \rangle^{(1)} dt = -\frac{1}{Q_N \beta} \int_0^{\tau} dt \int_0^{t} dt_1 \int d\mathcal{P}_0 d\mathcal{R}_0 \, e^{-\beta K} e^{-\beta U} \times$$

$$\times \nabla_{r_{10}} \left\{ \nabla_{\mathcal{R}_0 + (t-t_1) v_0} U(\mathcal{R}_0 + (t-t_1) v_0) \cdot \nabla_{\frac{\mathcal{R}_0 + (t-t_1)\mathcal{P}_0}{m}} \nabla_{r_{10} + t v_{10}} U \right\} \quad (54)$$

$$= -\frac{1}{\beta Q_N} \int_0^{\tau} dt \int_0^{t} dt_1 \int d\mathcal{P}_0 d\mathcal{R}_0 \, e^{-\beta K} e^{-\beta U} \, t_1 \times$$

$$\times \left\{ \nabla_{r_{10}} \nabla U \cdot \nabla\nabla U + \nabla U \cdot \nabla_{r_{10}} \nabla\nabla U \right\} . \quad (55)$$

We assume $U(\mathcal{R}) = \sum_{i<j} u_{ij}(r_{ij})$ and use the Fourier transform of $u$ :

$$u(r_{ij}) = \frac{1}{(2\pi)^3} \int \tilde{u}(k) e^{-i \vec{k} \cdot \vec{r}_{ij}} d^3k . \quad (56)$$

Each differentiation is equivalent to multiplication by $-i\vec{k}$ or $+i\vec{k}$, so equation 55 becomes:

$$\int_0^{T} dt \langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)} = -\frac{1}{\beta Q_N}\int_0^{\tau} dt \int_0^{t} dt_1 \int d\mathcal{P}_0\, d\mathcal{R}_0\, e^{-\beta K} e^{-\beta U} \times$$

$$\times \Bigg[ \int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3} \sum_{j=2}^{N} \exp\left\{ -i\vec{k}_1\cdot\left([t-t_1]\vec{v}_{10} - [t-t_1]\vec{v}_{j0} - i\vec{k}_2\cdot\left(t\vec{v}_{10} - t\vec{v}_{j0}\right)\right\} \times\right.$$

$$\times \exp\left\{ -i(\vec{k}_1+\vec{k}_2)\cdot\vec{r}_{1j}\right\} t_1\, \vec{k}_1\cdot\vec{k}_2\, \frac{m_1+m_j}{m_1 m_j}\left(\vec{k}_1\vec{k}_2 + \vec{k}_2\vec{k}_2\right)$$

$$+ \int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3} \sum_{\substack{k=2\\ k\neq j}}^{N} \sum_{j=2}^{N} \exp\left\{ -i\vec{k}_1\cdot\left([t-t_1]\vec{v}_{10} - [t-t_1]\vec{v}_{k0} - i\vec{k}_2\cdot\left(t\vec{v}_{10} - t\vec{v}_{j0}\right)\right\} \times\right.$$

$$\times \exp\left\{ -i\vec{k}_1\cdot\vec{r}_{1k} - i\vec{k}_2\cdot\vec{r}_{1j}\right\} t_1\, \frac{\vec{k}_1\cdot\vec{k}_2}{m_1}\left(-\vec{k}_1\vec{k}_2 + \vec{k}_2\vec{k}_2\right) .$$

$$+ \int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3} \sum_{\substack{l=2\\ l\neq j}}^{N} \sum_{j=2}^{N} \exp\left\{ -i\vec{k}_1\cdot\left([t-t_1]\vec{v}_{l0} - [t-t_1]\vec{v}_{j0}\right) - i\vec{k}_2\cdot\left(t\vec{v}_{10} - t\vec{v}_{j0}\right) \times\right.$$

$$\times \exp\left\{ -i\vec{k}_1\cdot\vec{r}_{lj} - i\vec{k}_2\cdot\vec{r}_{1j}\right\} t_1\, \frac{\vec{k}_1\cdot\vec{k}_2}{m_1}\left(\vec{k}_2\vec{k}_2\right) \Bigg] . \qquad (57)$$

We assume that the $\vec{k}$ integrations can be done after the ensemble averaging, instead of before.

We know that for equilibrium:

$$\left\langle \exp\left(-it\vec{k}\cdot\vec{v}\right)\right\rangle = \exp\left(-k^2t^2/2\beta m\right) \tag{58}$$

$$\left\langle \exp\left(-i\vec{k}\cdot\vec{r}_{ij}\right\rangle = \frac{1}{V}\left[\tilde{G}_{ij}(k) + (2\pi)^3\delta(\vec{k})\right], \tag{58a}$$

where $\tilde{G}_{ij}$ is the Fourier transform of $g_{ij}-1$ and $g_{ij}$ is the radial distribution function. In order to proceed, we must make some approximation for the terms involving two field particles (particles other than number 1). If we neglect correlation between the field particles, then

$$f^{(3)}(r_1,r_2,r_3) \longrightarrow \frac{1}{V^3}g(r_{12})g(r_{13}) \tag{59}$$

if 2 and 3 are field particles. Under this approximation

$$\begin{aligned}\left\langle e^{-i\vec{k}_1\cdot\vec{r}_{1k}}e^{-i\vec{k}_2\cdot\vec{r}_{1j}}\right\rangle \cong \frac{1}{V^2}\Big[&\tilde{G}_{1k}(k_1)\tilde{G}_{1j}(k_2)\\ &+(2\pi)^3\delta(\vec{k}_1)G_{1j}(k_2)+(2\pi)^3G_{1k}(k_1)\delta(\vec{k}_2)\\ &-(2\pi)^6\delta(\vec{k}_1)\delta(\vec{k}_2)\end{aligned} \tag{60}$$

and

$$\begin{aligned}\left\langle e^{-i\vec{k}_1\cdot\vec{r}_{\ell j}}e^{-i\vec{k}_2\cdot\vec{r}_{1j}}\right\rangle \cong \frac{1}{V^2}\Big[&\tilde{G}_{1\ell}(k_1)\tilde{G}_{1j}(\vec{k}_2+\vec{k}_1)\\ &+(2\pi)^3\tilde{G}_{1\ell}(k_1)\delta(\vec{k}_2+\vec{k}_1)+(2\pi)^3\delta(k_1)G_{1j}(\vec{k}_2+\vec{k}_1)\\ &+(2\pi)^6\delta(\vec{k}_1)\delta(\vec{k}_2).\end{aligned} \tag{61}$$

Note that we can leave out immediately all of the terms proportional to $\delta(\vec{k}_1)$ or $\delta(\vec{k}_2)$ since every integrand has the factor $\vec{k}_1 \cdot \vec{k}_2$. Equations 57-61 yield:

$$\int_0^\tau dt \langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)} = -\frac{1}{V\beta}\int_0^\tau dt \int_0^t dt_1\, t_1 \int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3} \times$$

$$\times \Bigg[ \sum_{j=2}^{N} G_{1j}(\vec{k}_1+\vec{k}_2)\,\tilde{u}(k_1)\tilde{u}(k_2)\exp\left\{-\frac{1}{2\beta\mu_j}\left[t(\vec{k}_1+\vec{k}_2)-t_1\vec{k}_1\right]^2\right\} \times$$

$$\times \frac{\vec{k}_1\cdot\vec{k}_2}{\mu_j}\left(\vec{k}_1\vec{k}_2+\vec{k}_2\vec{k}_2\right)$$

$$+\frac{1}{V}\sum_{\substack{k=2\\ k\neq j}}^{N}\sum_{j=2}^{N} \tilde{G}_{1k}(k_1)\tilde{G}_{1j}(k_2)\,\tilde{u}(k_1)\tilde{u}(k_2)\exp\left\{-\frac{1}{2\beta m_1}\times\right.$$

$$\left.\times\left[t(\vec{k}_1+\vec{k}_2)-t_1\vec{k}_1\right]^2\right\}\exp\left\{-\frac{1}{2\beta m_k}\left[(t-t_1)k_1\right]^2\right\}\exp\left\{-\frac{1}{2\beta m_j}t^2k_2^2\right\}\times$$

$$\times \frac{\vec{k}_1\cdot\vec{k}_2}{m_1}\left(-\vec{k}_1\vec{k}_2+\vec{k}_2\vec{k}_2\right)$$

$$+\frac{1}{V}\sum_{\substack{l=2\\ l\neq j}}^{N}\sum_{j=2}^{N}\left[\tilde{G}_{1l}(k_1)\tilde{G}_{1j}(\vec{k}_1+\vec{k}_2)+(2\pi)^3\tilde{G}_{1l}(k_1)\delta(\vec{k}_1+\vec{k}_2)\right]\times$$

$$\times\tilde{u}(k_1)\tilde{u}(k_2)\exp\left\{-\frac{1}{2\beta m_1}\left[t(\vec{k}_1+\vec{k}_2)-t_1\vec{k}_1\right]^2\right\}\times$$

$$\times\exp\left\{-\frac{1}{2\beta m_l}\left[(t-t_1)k_1\right]^2\right\}\exp\left\{-\frac{1}{2\beta m_j}t^2k_2^2\right\}\times$$

$$\times\frac{\vec{k}_1\cdot\vec{k}_2}{m_j}\left(\vec{k}_2\vec{k}_2\right)\Bigg] \quad , \qquad (62)$$

where $\mu_{\alpha\beta}$ is the reduced mass, $m_\alpha m_\beta/(m_\alpha+m_\beta)$.

The three double time integrals in equation 62 are of the same form:

$$I_\alpha = \int_0^\tau dt \int_0^t dt_1\, t_1\, e^{-C_\alpha t^2} e^{-(A_\alpha^2 t_1^2 - 2B_\alpha t_1 t)} \tag{63}$$

where the $A_\alpha, B_\alpha, C_\alpha$ are functions of $k_1, k_2, m_i, m_j,$ $m_k$ and $m_l$, but independent of $t$ and $t_1$.

Completing the square gives:

$$I_\alpha = \int_0^\tau dt\, e^{-C_\alpha t^2 + B_\alpha^2 t^2/A_\alpha^2} \int_0^t dt_1\, t_1\, e^{-(A_\alpha t_1 - \frac{B_\alpha}{A_\alpha} t)^2} . \tag{64}$$

Call the $t_1$ integral $I_\alpha^a$ and let $A_\alpha t_1 - \frac{B_\alpha}{A_\alpha} t = X$ :

$$I_\alpha^a = \frac{1}{A_\alpha^2} \int_{-B_\alpha t/A_\alpha}^{t(A_\alpha - B_\alpha/A_\alpha)} \left(X + \frac{B_\alpha t}{A_\alpha}\right) e^{-X^2} dX \tag{65}$$

$$= \frac{-1}{2A_\alpha^2}\left[e^{-t^2(A_\alpha - B_\alpha/A_\alpha)^2} - e^{-t^2 B_\alpha^2/A_\alpha^2}\right]$$

$$+ \frac{t B_\alpha}{2A_\alpha^3}\sqrt{\pi}\left[\operatorname{erf}\left[t\left(A_\alpha - \frac{B_\alpha}{A_\alpha}\right)\right] - \operatorname{erf}\left[-\frac{t B_\alpha}{A_\alpha}\right]\right]. \tag{66}$$

Now

$$I_\alpha = \int_0^\tau dt \exp\left(-C_\alpha t^2 + \frac{B_\alpha^2 t^2}{A_\alpha^2}\right)\left\{\frac{-1}{2A_\alpha^2}\left[e^{-t^2\left(A_\alpha - \frac{B_\alpha}{A_\alpha}\right)^2}\right.\right.$$

$$\left.\left. - e^{-t^2 B_\alpha^2/A_\alpha^2}\right] + \frac{t B_\alpha}{2A_\alpha^3}\sqrt{\pi}\left[\operatorname{erf}\left[t\left(A_\alpha - \frac{B_\alpha}{A_\alpha}\right)\right] - \operatorname{erf}\left[-\frac{t B_\alpha}{A_\alpha}\right]\right]\right\}. \tag{67}$$

The first two terms can be integrated to give error functions, but the last two are like:

$$I_\alpha^{\,b} = \int_0^\tau t\, e^{-F_\alpha t^2} \int_0^{E_\alpha t} e^{-t'^2}\, dt'\, dt \quad , \qquad (68)$$

where the $E_\alpha$ and $F_\alpha$ are functions of $B_\alpha$ and $A_\alpha$. Equation 68 can be simplified by a partial integration to yield

$$\begin{aligned} I_\alpha^{\,b} &= -\frac{1}{4F_\alpha}\sqrt{\pi}\, \mathrm{erf}\,(E_\alpha \tau) \\ &\quad + \frac{E_\alpha}{4F_\alpha}\sqrt{\frac{\pi}{F_\alpha + E_\alpha^2}}\, \mathrm{erf}\left(\sqrt{F_\alpha + E_\alpha^2}\,\tau\right) . \end{aligned} \qquad (69)$$

Thus $I_\alpha$ is given by

$$\begin{aligned} I_\alpha = \frac{1}{2A_\alpha^2}\Bigg[ & \frac{-1}{2}\sqrt{\pi}\, \frac{1}{\sqrt{C_\alpha + A_\alpha^2 - 2B_\alpha}}\, \mathrm{erf}\left(\sqrt{C_\alpha + A_\alpha^2 - 2B_\alpha}\right) \\ & + \frac{1}{2}\sqrt{\pi}\, \frac{1}{\sqrt{C_\alpha}}\, \mathrm{erf}\left(\sqrt{C_\alpha}\,\tau\right) \\ & + \frac{\sqrt{\pi}\, B_\alpha}{4A_\alpha^3 (C_\alpha - B_\alpha^2 / A_\alpha^2} \Bigg\{ e^{-F_\alpha t^2} \left( \mathrm{erf}\left[\left(A_\alpha - \frac{B_\alpha}{A_\alpha}\right)\tau\right] - \mathrm{erf}\left[-\frac{B_\alpha \tau}{A_\alpha}\right] \right) \\ & + \frac{(A_\alpha - B_\alpha / A_\alpha)}{\sqrt{C_\alpha + A_\alpha^2 - 2B_\alpha}}\, \mathrm{erf}\left(\sqrt{C_\alpha + A_\alpha^2 - 2B_\alpha}\,\tau\right) \\ & + \frac{B_\alpha / A_\alpha}{\sqrt{C_\alpha}}\, \mathrm{erf}\left(\sqrt{C_\alpha}\,\tau\right) \Bigg\} . \end{aligned} \qquad (70)$$

In the foregoing, $A_\alpha$, $B_\alpha$ and $C_\alpha$ are given by:

$$A_1^2 = \frac{k_1^2}{2\beta\mu_{ij}}$$

$$B_1 = \vec{k}_1 \cdot (\vec{k}_1 + \vec{k}_2)$$

$$C_1 = \frac{(\vec{k}_1 + \vec{k}_2)^2}{2\beta\mu_{ij}}$$

$$A_2^2 = k_1^2\left(\frac{1}{2\beta\mu_{ij}} + \frac{1}{2\beta m_k}\right)$$

$$B_2 = \frac{\vec{k}_1 \cdot (\vec{k}_1 + \vec{k}_2)}{2\beta\mu_{ij}} + \frac{k_1^2}{2\beta m_k}$$

$$C_2 = \frac{(\vec{k}_1 + \vec{k}_2)^2}{2\beta\mu_{ij}} + \frac{k_2^2}{2\beta m_j} + \frac{k_1^2}{2\beta m_k}$$

$$A_3^2 = k_1^2\left(\frac{1}{2\beta\mu_{ij}} + \frac{1}{2\beta m_l}\right)$$

$$B_3 = \frac{\vec{k}_1 \cdot (\vec{k}_1 + \vec{k}_2)}{2\beta\mu_{ij}} + \frac{k_1^2}{2\beta m_l}$$

$$C_3 = \frac{(\vec{k}_1 + \vec{k}_2)^2}{2\beta\mu_{ij}} + \frac{k_2^2}{2\beta m_j} + \frac{k_1^2}{2\beta m_l}$$

and

$$F_\alpha = C_\alpha - B_\alpha^2/A_\alpha \quad . \qquad (71)$$

Our 1st order correction to the friction coefficient is now proportional to:

$$
\begin{aligned}
\int_0^{\tau}\langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)}dt = -\frac{1}{\beta V}\int\frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3}\Big[\sum_{j=2}^{N}\tilde{G}_{1j}(\vec{k}_1+\vec{k}_2)\,\times \\
\times\,\tilde{u}(k_1)\tilde{u}(k_2)\frac{\vec{k}_1\cdot\vec{k}_2}{\mu_{1j}}\left(\vec{k}_1\vec{k}_2+\vec{k}_2\vec{k}_2\right)I_1 \\
+\frac{1}{V}\sum_{k=2}^{N}\sum_{j=2}^{N}\tilde{G}_{1k}(k_1)\tilde{G}_{1j}(k_2)\tilde{u}(k_1)\tilde{u}(k_2)\,\times \\
\times\,\frac{\vec{k}_1\cdot\vec{k}_2}{m_1}\left(-\vec{k}_1\vec{k}_2+\vec{k}_2\vec{k}_2\right)I_2 \\
+\frac{1}{V}\sum_{\substack{l=2\\ l\neq j}}^{N}\sum_{j=2}^{N}\Big[\tilde{G}_{1l}(k_1)\tilde{G}_{1j}(\vec{k}_2+\vec{k}_1)+(2\pi)^3\tilde{G}_{1l}(k_1)\delta(\vec{k}_2+\vec{k}_1)\Big]\times \\
\times\,\tilde{u}(k_1)\tilde{u}(k_2)\frac{\vec{k}_1\cdot\vec{k}_2}{m_j}\left(\vec{k}_2\vec{k}_2\right)I_3\quad .
\end{aligned}
\tag{72}
$$

Now that the time integrals have been evaluated, we have proceeded as far as we can without choosing a particular potential and substituting actual functions into equation 72 for $\tilde{u}(k)$ and $\tilde{G}(k)$. In other words, equation 72 is our result for a general potential. Since the $I_\alpha$ are fairly complicated, we make the same approximation used by Helfand in his zero-order term, that of letting $\tau\rightarrow\infty$. If all orders were included, this should force $\zeta$ to vanish, but it does not make $\zeta^{(0)}$ and $\zeta^{(1)}$ vanish, so the lower orders taken by themselves may be meaningful, and at least it is of interest to compare

$$\lim_{\tau\to\infty} \frac{1}{\tau}\int_0^\tau \langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(1)} dt$$

with

$$\lim_{\tau\to\infty} \frac{1}{\tau}\int_0^\tau \langle \vec{F}_1(0)\vec{F}_1(t)\rangle^{(0)} dt ,$$

which is Helfand's linear trajectory approximation.

In this limit, equation 70 becomes

$$\lim_{\tau\to\infty} I_\alpha(\tau) = \frac{\sqrt{\pi}}{4A_\alpha^2}\,\frac{\left(-C_\alpha+\sqrt{A_\alpha^2-2B_\alpha+C_\alpha}\sqrt{C_\alpha}+B_\alpha\right)}{\left(C_\alpha-B_\alpha^2/A_\alpha^2\right)\sqrt{A_\alpha^2-2B_\alpha+C_\alpha}} , \qquad (73)$$

and equation 72, of course, retains the same form.

Substitution of the constants from equation 71 into equation 73 gives

$$I_1(\infty) = \frac{\sqrt{\pi/2}}{\dfrac{k_1^2 k_2}{(\beta\mu_j)^{3/2}}}\left[\frac{-k_2^2-k_1k_2\cos\gamma+k_2\sqrt{k_1^2+2k_1k_2\cos\gamma+k_2^2}}{\left(k_1^2+2k_1k_2\cos\gamma+k_2^2\right)\left(1-\cos\gamma\right)}\right], \qquad (74)$$

where $k_1 = |\vec{k}_1|$ , $k_2 = |\vec{k}_2|$ , and $\gamma$ is the angle between the vectors $\vec{k}_1$ and $\vec{k}_2$ :

$$\cos\gamma = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2). \qquad (75)$$

For $I_2(\infty)$ we obtain:

$$I_2(\infty) = \begin{array}{c}\sqrt{\pi/2} \\ \frac{k_1^2 k_2}{\beta^{3/2}} \frac{1}{M_{ijk}} \sqrt{\frac{1}{M_{ijj}}}\end{array} \left[ \frac{-\frac{k_1 k_2 \cos\gamma}{\mu_{ij}} - \frac{k_2^2}{M_{ijj}} + k_2 \sqrt{\frac{1}{M_{ijj}} \left( \frac{k_1^2}{M_{ijk}} + \frac{2k_1 k_2 \cos\gamma}{\mu_{ij}} + \frac{k_2^2}{M_{ijj}} \right)}}{\frac{k_1^2}{M_{ijk}} + \frac{2k_1 k_2 \cos\gamma}{\mu_{ij}} + \frac{k_2^2}{M_{ijj}} - \frac{\left( \frac{k_1^2}{M_{ijk}} + k_1 k_2 \cos\gamma \right)^2}{k_1^2 / M_{ijk}}} \right] \qquad (76)$$

where we define

$$\frac{1}{M_{\alpha\beta\gamma}} = \frac{1}{m_\alpha} + \frac{1}{m_\beta} + \frac{1}{m_\gamma} \quad . \qquad (77)$$

$I_3(\infty)$ is identical, except that the index $k$ is replaced everywhere by $l$ .

Now, in order to proceed further, we must substitute $\tilde{G}$ and $\tilde{u}$ for some specific potential and integrate over $k_1$ and $k_2$ . If we consider the case of a coulomb potential without short-range potentials and a system sufficiently dilute that the Debye-Hückel radial distribution function can be used,

$$\tilde{G}_{\alpha\beta}(k) = -4\pi z_\alpha z_\beta \epsilon^2 \beta \frac{1}{k^2 + \kappa^2} \qquad (78)$$

and

$$\tilde{u}_{\alpha\beta}(k) = 4\pi z_\alpha z_\beta \epsilon^2 \frac{1}{k^2} \quad , \qquad (79)$$

where $\kappa$ is the Debye-Hückel inverse length,

$$\kappa^2 \equiv 4\pi \epsilon^2 \beta \sum_{s=1}^{\sigma} c_s z_s^2 \quad . \qquad (80)$$

Here $c_s$ is the concentration of particles of type $s$ in units of particles per unit volume, and $z_s$ is their charge.

This case corresponds to a dilute plasma which is sufficiently hot that all of the ions are stripped of all their electrons. Other cases can be considered, including that of systems far enough from equilibrium that the equilibrium distribution functions cannot be used. Substitution of equations 74, 75, 76, 78, and 79 into equation 72 and integration over $\vec{k}_1$ and $\vec{k}_2$ yield our first-order correction to the Fokker-Planck coefficient, but this integration will not be carried through in this thesis.

### b. Momentum Autocorrelation Function

We now apply the perturbation series of equations 44-46 to the calculation of a one-body momentum autocorrelation function, $\langle \vec{p}_1(0)\, \vec{p}_1(t) \rangle$ .

First, the zero order term is just the same as the linear trajectory approximation, so

$$\langle \vec{p}_1(0)\, \vec{p}_1(t) \rangle^{(0)} = \langle \vec{p}_1(0)\, \vec{p}_1(0) \rangle \tag{81}$$

which at equilibrium is $\underset{\approx}{1}\, mkT$ . We look first at the simplest case, in which we use the equilibrium distribution function and neglect correlations between field particles.

The first-order correction is:

$$\langle \vec{p}_1(0)\vec{p}_1(t) \rangle^{(1)} = \int f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; 0)\, \vec{p}_{10} \int_0^t dt_1\, \vec{F}_1(\mathcal{R}_0 + (t-t_1)\mathcal{V}_0)\, d\mathcal{R}_0\, d\mathcal{P}_0 \,, \tag{82}$$

or for pair potentials,

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} =$$

$$= -\int f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;0)\vec{p}_{10}\int_0^t \nabla_{r_{10}} \sum_{j=2}^{N} u_{j}\left(|\vec{r}_{10}-\vec{r}_{j0}+(t-t_1)\vec{v}_{10}-(t-t_1)\vec{v}_{j0}|\right) d\mathcal{R}_0\, d\mathcal{P}_0 . \qquad (83)$$

Using the Fourier transform of $u$, equation 83 becomes

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} = \frac{i}{(2\pi)^3}\sum_{j=2}^{N}\int d\mathcal{R}_0\, d\mathcal{P}_0\, f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;0)\,\vec{p}_{10}\int_0^t dt_1 \times$$

$$\times \int d^3k\, u_{1j}(k)\,\vec{k}\, e^{-i\vec{k}\cdot\vec{r}_{1j}}\, e^{-i\vec{k}\cdot(t-t_1)\vec{v}_{10}}\, e^{i\vec{k}\cdot(t-t_1)\vec{v}_{j0}} . \qquad (84)$$

At equilibrium, the momentum separates and we can average the functions of the separate velocities separately. Averaging the real and imaginary parts, we find that

$$\left\langle \mathrm{Im}\left\{ i m \vec{v}_{10}\, e^{-i\vec{k}\cdot(t-t_1)\vec{v}_{10}} \right\} \right\rangle$$

vanishes, as it must, and that $\left\langle \mathrm{Re}\left\{ i m \vec{v}_{10}\, e^{-i\vec{k}\cdot(t-t_1)\vec{v}_{10}} \right\} \right\rangle$ can be shown with some effort to equal

$$\frac{1}{\beta}(t-t_1)\vec{k}\, \exp\left\{-\frac{1}{2\beta m_1}(t-t_1)^2 k^2\right\} . \qquad (85)$$

Also, as before,

$$\left\langle e^{-i(t-t_1)\vec{k}\cdot\vec{v}_{j0}} \right\rangle = \exp\left\{\frac{-1}{2\beta m_j}(t-t_1)^2 k^2\right\}, \qquad (86)$$

and

$$\left\langle e^{i\vec{k}\cdot\vec{r}_{1j}} \right\rangle = \frac{1}{V}\left[\tilde{G}_{1j}(k) + (2\pi)^3\delta(\vec{k})\right] . \qquad (87)$$

Using these, we find for the first-order correction

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} = \frac{1}{(2\pi)^3\beta V}\int_0^t dt_1 \sum_{j=2}^{N}\int d^3k\, \hat{u}(k)\, \vec{k}\vec{k} \times (t-t_1)\exp\left\{-\frac{(t-t_1)^2k^2}{2\beta\mu_{1j}}\right\}\tilde{G}_{1j}(k) \quad (88)$$

The time integration must now be done. We let

$$I = \int_0^t dt_1\,(t-t_1)\exp\left\{-\frac{k^2}{2\beta\mu_{1j}}(t-t_1)^2\right\} = -\int_t^0 dt'\,t'\exp\left\{-\frac{k^2}{2\beta\mu_{1j}}t'^2\right\}, \quad (89)$$

where $t' = t - t_1$, and we now let $t_0 = 0$.

We find

$$I = \frac{-\beta\mu_{1j}}{k^2}\left[\exp\left\{-\frac{k^2t^2}{2\beta\mu_{1j}}\right\} - 1\right], \quad (90)$$

so now

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} = \frac{-1}{(2\pi)^3\beta V}\sum_{j=2}^{N}\int d^3k\, \vec{k}\vec{k}\,\tilde{u}(k) \times \frac{\beta\mu_{1j}}{k^2}\left[\exp\left\{\frac{-k^2t^2}{2\beta\mu_{1j}}\right\} - 1\right] . \quad (91)$$

Look at the simplest case again, with the Debye-Hückel radial distribution function and the coulomb potential without short-range repulsion:

$$\tilde{u}_{1j}(k) = \frac{4\pi z_1 z_j \epsilon^2}{k^2} \;;\; \tilde{G}_{1j}(k) = \frac{-4\pi z_1 z_j \epsilon^2\beta}{k^2+\kappa^2} . \quad (92)$$

We now have

$$\left\langle \vec{p}_1(t)\vec{p}_1(0)\right\rangle^{(1)} = \frac{2z_1^2 e^4\beta}{\pi V}\sum_{j=2}^{N} z_j^2 \mu_{1j}\int d^3k\,\frac{\vec{k}\vec{k}}{k^2}\;\times$$

$$\times\;\frac{1}{k^2}\,\frac{1}{k^2+\kappa^2}\left[\exp\left\{-\frac{k^2t^2}{2\beta\mu_{1j}}\right\}-1\right]. \tag{93}$$

This can be shown to equal, for sufficiently large N:

$$-\underset{\approx}{1}\;\frac{8z_1^2e^4\beta}{3}\sum_{s=1}^{\sigma} z_s^2 c_s \mu_{1s}\left[\frac{\pi}{2\kappa}-\mathcal{Q}_s\right], \tag{94}$$

where $C_s$ is the concentration of species $s$ , and $\mathcal{Q}_s$ is the integral

$$\mathcal{Q}_s = \int_0^\infty \frac{dk}{k^2+\kappa^2}\exp\left\{\frac{-k^2t^2}{2\beta\mu_{1s}}\right\}. \tag{95}$$

This integral can be evaluated as follows (29): We use the identity

$$\frac{1}{\kappa^2+k^2} = \frac{1}{2\kappa}\int_{-\infty}^{\infty} e^{ikx}\,e^{-\kappa|x|}\,dx \quad , \tag{96}$$

from which

$$\mathcal{Q}_s = \frac{1}{4\kappa}\int_{-\infty}^{\infty}dk\int_{-\infty}^{\infty}dx\,e^{-a_s k^2+ikx-\kappa|x|} \quad , \tag{97}$$

where $a_s = t^2/2\beta\mu_{1s}$ . Completing the square, one finds

$$\mathcal{Q}_s = \frac{1}{4\kappa}\sqrt{\frac{\pi}{a_s}}\int_{-\infty}^{\infty} e^{-\frac{x^2}{4a_s}-\kappa|x|}\,dx \quad , \tag{98}$$

which gives after again completing a square:

$$\mathcal{J}_s = \frac{\pi e^{a_s \kappa^2}}{2\kappa}\left[1 - \mathrm{erf}(\sqrt{a_s}\,\kappa)\right] . \tag{99}$$

From equation 94, we now have

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} = -\underset{\approx}{1}\,\frac{8 z_1^2 \epsilon^4 \beta}{3} \sum_{s=1}^{\sigma} z_s^2 \mu_{1s} \times$$

$$\times\left[\frac{\pi}{2\kappa}\left(1 - e^{-t^2\kappa^2/2\beta\mu_{1s}} + e^{-t^2\kappa^2/2\beta\mu_{1s}}\,\mathrm{erf}\left(t\kappa/\sqrt{2\beta\mu_{1s}}\right)\right)\right]. \tag{100}$$

This has exactly the behaviour we would expect, vanishing at $t \to 0$, as the linear trajectory approximation becomes valid, becoming negative for all times $t > 0$, and attaining an asymptotic value depending on $z_1, \beta, \kappa, z_s$ and $\mu_{1s}$ for $s = 1, 2, \cdots, \sigma$:

$$\lim_{t\to\infty} \langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(1)} = -\underset{\approx}{1}\,\frac{4\pi z_1^2 \epsilon^4 \beta}{3\kappa} \sum_{s=1}^{\sigma} z_s^2 \mu_{1s} . \tag{101}$$

Now we turn our attention to the second-order correction to $\langle \vec{p}_1(0)\vec{p}_1(t)\rangle$. The entire argument proceeds as before, except that there are two time integrations, two $k$ integrations, and attendant complications.

From equations 44 and 46, we have

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)} = \int_0^t dt_1 \int_0^{t_1} dt_2\, \vec{p}_{10}\, f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; 0)\,\Omega^{(0)}(t,t_1) \times$$

$$\times\ \vec{F}\cdot\nabla_{\mathcal{P}_0}\Omega^{(0)}(t_2,0)\,\vec{p}_{10}\, d\mathcal{R}_0\, d\mathcal{P}_0 . \tag{102}$$

This simplifies to:

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle = \int_0^t dt_1 \int_0^{t_1} dt\, \vec{p}_{10}\, f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; 0)\, \Omega^{(0)}(t,t_1)\, \vec{F}\cdot\nabla_{\mathcal{P}_0} \times$$
$$\times\ \vec{F}_1(\mathcal{R}_0 + (t_1 - t_2)v_0)\, d\mathcal{R}_0\, d\mathcal{P}_0 \tag{103}$$

We replace $\nabla_{\mathcal{P}_0}\vec{F}_1(\mathcal{R}_0 + (t_1-t_2)v_0)$ with $(t_1-t_2)\underset{m}{\underline{\nabla_{\mathcal{R}}}}\cdot\ \vec{F}_1(\mathcal{R}_0 + (t_1-t_2)\mathcal{P}_0/m)$ as we did in the case of the Fokker-Planck coefficient. We also assume that the forces can be derived from pair potentials, and obtain

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)} = \int \vec{p}_{10}\, f^{(N)}(\mathcal{R}_0, \mathcal{P}_0; 0) \int_0^t dt_1 \int_0^{t_1} dt_2\, (t_1 - t_2) \times$$
$$\times \sum_{\substack{i=1 \\ i<j}}^{N} \nabla_{r_i'} \sum_{j=1}^{N} u(r_{ij}') \cdot \sum_{i=1}^{N} \frac{1}{m_i} \nabla_{r_i'} \nabla_{r_1''} \sum_{n=2}^{N} u(r_{1n}'')\, d\mathcal{R}_0\, d\mathcal{P}_0, \tag{104}$$

where $\mathcal{R}' = \mathcal{R}_0 + (t-t_1)\mathcal{P}_0/m$ and

$$\mathcal{R}'' = \mathcal{R}' + (t_1 - t_2)\mathcal{P}_0/m = \mathcal{R}_0 + (t - t_2)\mathcal{P}_0/m .$$

Now we express the potentials as Fourier integrals as before, and obtain the following result (since we have broken up 3N-dimensional vectors into sums of 3-dimensional vectors, we include 3-dimensional unit vectors $\hat{e}_\alpha$ for clarity):

$$\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)} = \frac{i}{(2\pi)^6}\int dR_0\, dP_0\, \vec{p}_{10}\, f^{(N)}(R_0, P_0; 0) \;\times$$

$$\times \int_0^t dt_1 \int_0^{t_1} dt_2\, (t_1 - t_2)\Bigg[\frac{1}{m_1}\sum_{j=2}^{N}\sum_{n=2}^{N} \hat{e}_1 \int d^3k_1\, \vec{k}_1\, \tilde{u}(k_1)\, e^{-i\vec{k}_1\cdot\vec{r}'_{1j}} \,\cdot$$

$$\cdot\, \hat{e}_1\hat{e}_1 \int d^3k_2\, \vec{k}_2\vec{k}_2\, \tilde{u}(k_2)\, e^{-i\vec{k}_2\cdot\vec{r}''_{1n}}$$

$$- \sum_{n=2}^{N}\sum_{\substack{j=2\\ n\neq j}}^{N} \frac{\hat{e}_n}{m_n}\int d^3k_1\, \vec{k}_1\, \tilde{u}(k_1)\, e^{-i\vec{k}_1\cdot\vec{r}'_{nj}} \,\cdot \tag{105}$$

$$\cdot\, \hat{e}_n\hat{e}_1 \int d^3k_2\, \vec{k}_2\vec{k}_2\, \tilde{u}(k_2)\, e^{-i\vec{k}_2\cdot\vec{r}''_{1n}}\Bigg] .$$

We now mean by this notation that $\hat{e}_\alpha \vec{k}_\beta$ is a vector, not a tensor, but that its three components lie in the subspace of particle $\alpha$. We interchange the order of the k integrations and ensemble averaging, and again restrict ourselves, for the purpose of this calculation, to the case of equilibrium distribution functions, and in addition we again neglect correlations between field particles. The ensemble averages involved are the same as those encountered before in equations 58, 58a, 60, 61, and 85. Using these results and separating the terms for $n = j$ and $n \neq j$, we obtain:

$$\langle \vec{p}_1(0)\,\vec{p}_1(t)\rangle^{(2)} = \frac{1}{V^2\beta}\sum_{j=2}^{N}\sum_{\substack{n=2\\ j\neq n}}^{N}\int \frac{d^3k_1}{(2\pi)^3}\,\frac{d^3k_2}{(2\pi)^3}\,(\vec{k}_1\cdot\vec{k}_2)\times$$

$$\times\,\vec{k}_2\,\tilde{u}(k_1)\,\tilde{u}(k_2)\Big[\frac{1}{m_1}\tilde{G}_{1j}(k_1)\,\tilde{G}_{1n}(k_2)\, I_4$$

$$+\,\frac{\delta_{jn}V}{m_1}\,G_{1j}(\vec{k}_2+\vec{k}_1)\; I_5 \tag{106}$$

$$-\,\frac{1}{m_1}\Big\{\tilde{G}_{1j}(k_1)\,\tilde{G}_{1n}(\vec{k}_2+\vec{k}_1)+(2\pi)^3\,\tilde{G}_{1j}(k_1)\,\delta(\vec{k}_2+\vec{k}_1)\Big\} I_6\Big],$$

where the $I_\alpha$ are double time integrals, and are functions of $t, k_1, k_2, \beta, m_1, m_j$ and $m_n$. If we write them as integrals over $\tau_1 = t - t_1$, and $\tau_2 = t - t_2$, they are:

$$I_4(t) = \int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2\,(\tau_2-\tau_1)(\vec{k}_1\tau + \vec{k}_2\tau_2)\, e^{-D_4^2\tau_1^2}\, e^{-E_4^2\tau_2^2 - 2F_4\tau_1\tau_2} \tag{107}$$

$$I_5(t) = \int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2\,(\tau_2-\tau_1)(\vec{k}_1\tau_1 + \vec{k}_2\tau_2)\, e^{-D_5^2\tau_1^2}\, e^{-E_5^2\tau_2^2 - 2F_5\tau_1\tau_2} \tag{108}$$

$$I_6(t) = \int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2\,(\tau_2-\tau_1)\,\vec{k}_2\tau_2\, e^{-D_6^2\tau_1^2}\, e^{-E_6^2\tau_2^2 - 2F_6\tau_1\tau_2}, \tag{109}$$

where the $D, E$ and $F$ are as follows:

$$D_4^2 = \frac{k_1^2}{2\beta\mu_{1j}}, \quad E_4^2 = \frac{k_2^2}{2\beta\mu_{1j}}, \quad F_4 = \frac{k_1 \cdot k_2}{2\beta m_1},$$

$$D_5^2 = \frac{1}{2\beta\mu_{1j}}\left(k_1^2 + k_1 \cdot k_2\right), \quad E_5^2 = \frac{k_2^2}{2\beta\mu_{1j}}, \quad F_5 = \frac{k_1 \cdot k_2}{2\beta\mu_{1j}}, \tag{110}$$

$$D_6^2 = \frac{k_1^2}{2\beta\mu_{jn}}, \quad E_6^2 = \frac{k_2^2}{2\beta\mu_{1n}}, \quad F_6 = \frac{\vec{k}_1 \cdot \vec{k}_2}{2\beta m_n}.$$

A completion of squares and change of variables gives:

For $\alpha = 4, 5$:

$$\begin{aligned} I_\alpha(t) = {} & \Big[ -\vec{k}_1\left(\frac{F_\alpha}{E_\alpha^3} + \frac{1}{E_\alpha}\right) + \vec{k}_2\left(\frac{F_\alpha^2}{E_\alpha^5} + \frac{F_\alpha}{E_\alpha^3}\right) Q_1^\alpha \\ & + \left[\frac{\vec{k}_1}{E_\alpha^2} - \vec{k}_2\left(\frac{2F_\alpha}{E_\alpha^4} + \frac{1}{E_\alpha^2}\right)\right] Q_2^\alpha \\ & + \frac{\vec{k}_2}{E_\alpha^3}\, Q_3^\alpha \end{aligned} \tag{111}$$

,

and for $\alpha = 6$ :

$$I_6(t) = \vec{k}_2 \Big[ \Big( \frac{F_6^2}{E_6^5} + \frac{F_6}{E_6^3} \Big) Q_1^6 \qquad , \qquad (112)$$

$$+ \Big( \frac{2F_6}{E_6^4} - \frac{1}{E_6^2} \Big) Q_2^6$$

$$+ \frac{1}{E_6^3} Q_3^6 \Big] .$$

Here

$$Q_1^\alpha = \int_0^t d\tau_1 \hat{\tau}_1^2 e^{-G_\alpha^2 \hat{\tau}_1^2} \int_{(E_\alpha + H_\alpha)\hat{\tau}_1}^{E_\alpha t + H_\alpha \hat{\tau}_1} e^{-x^2} dx \, , \qquad (113)$$

$$Q_2^\alpha = \int_0^t d\tau_1 \tau_1 e^{-G_\alpha^2 \hat{\tau}_1^2} \int_{(E_\alpha + H_\alpha)\hat{\tau}_1}^{E_\alpha t + H_\alpha \hat{\tau}} x e^{-x^2} dx \, , \qquad (114)$$

and

$$Q_3^\alpha = \int_0^t d\tau_1 e^{-G_\alpha^2 \hat{\tau}_1^2} \int_{(E_\alpha + H_\alpha)\hat{\tau}_1}^{E_\alpha t + H_\alpha \hat{\tau}_1} x^2 e^{-x^2} dx \, , \qquad (115)$$

where $G_\alpha^2 = D_\alpha^2 - F_\alpha^2 / E_\alpha^2 = D_\alpha^2 - H_\alpha^2$

and $H_\alpha = F_\alpha / E_\alpha .$

If $N$ and $V$ are large, it is worthwhile to rewrite the sums in equation 106 so that they run over the chemical species present. We now do so, neglecting the distinction between $N_\alpha$, $N_\alpha - 1$, and $N_\alpha - 2$ where $N_\alpha$ is the number of particles of species $\alpha$ in the system. We let $c_\alpha = N_\alpha / V$, and write:

$$\begin{aligned}
\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)} = {} & \frac{1}{\beta}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma} c_\alpha c_\beta \int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3}\,\vec{k}_1\cdot\vec{k}_2\,\vec{k}_2 \,\times \\
& \times\, \tilde{u}(k_1)\,\tilde{u}(k_2)\Bigg[\frac{1}{m_1}\tilde{G}_{1\alpha}(k_1)\,\tilde{G}_{1\beta}(k_2)\Bigg\{\Bigg(-\vec{k}_1\left[\frac{F_4}{E_4^3}+\frac{1}{E_4}\right]+ \\
& +\vec{k}_2\left[\frac{F_4^2}{E_4^5}+\frac{F_4}{E_4^3}\right]\Bigg)\mathcal{Q}_1^4+\left(\frac{\vec{k}_1}{E_4^2}-\vec{k}_2\left[\frac{2F_4}{E_4^4}+\frac{1}{E_4^2}\right]\right)\mathcal{Q}_2^4+\frac{\vec{k}_2}{E_4^2}\mathcal{Q}_3^4\Bigg\} \\
& +\frac{\delta_{\alpha\beta}}{m_1 c_\beta}\tilde{G}_{1\alpha}(\vec{k}_1+\vec{k}_2)\Bigg\{\Bigg(-\vec{k}_1\left[\frac{F_5}{E_5^3}+\frac{1}{E_5}\right]+\vec{k}_2\left[\frac{F_5^2}{E_5^5}+\frac{F_5}{E_5^3}\right]\Bigg)\mathcal{Q}_1^5 \\
& +\left(\frac{\vec{k}_1}{E_5^2}-\vec{k}_2\left[\frac{2F_5}{E_5^4}+\frac{1}{E_5^2}\right]\right)\mathcal{Q}_2^5+\frac{\vec{k}_2}{E_5^3}\mathcal{Q}_3^5\Bigg\} \qquad (116) \\
& -\frac{1}{m_\beta}\tilde{G}_{1\alpha}(k_1)\,\tilde{G}_{1\beta}(\vec{k}_1+\vec{k}_2)\Bigg\{\vec{k}_2\left(\frac{F_6^2}{E_6^5}+\frac{F_6}{E_6^3}\right)\mathcal{Q}_1^6-\vec{k}_2\left(\frac{2F_6}{E_6^4}+\frac{1}{E_6^2}\right)\mathcal{Q}_2^6 \\
& +\frac{\vec{k}_2}{E_6^3}\mathcal{Q}_3^6\Bigg\}\Bigg]-\frac{1}{\beta}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\frac{c_\alpha c_\beta}{m_\beta}\int\frac{d^3k_1}{(2\pi)^3}\,k_1^2\,\vec{k}_1\vec{k}_1\left[\tilde{u}(k_1)\right]^2\times \\
& \times\,\tilde{G}_{1\alpha}(k_1)\left\{-\left(\frac{F_6'^2}{E_6'^5}+\frac{F_6'}{E_6'^3}\right)\mathcal{Q}_1^{6'}+\left(2\frac{F_6'}{E_6'^4}+\frac{1}{E_3'^2}\right)\mathcal{Q}_2^{6'}-\frac{1}{E_6'^3}\mathcal{Q}_3^{6'}\right\},
\end{aligned}$$

where we have separated off the term with the delta function factor and performed the $\vec{k}_2$ integration. The primes indicate that in the primed functions $\vec{k}_2$ has been replaced by $-\vec{k}_1$. We will find that the factor in curly brackets in this term is proportional to $|k_1|^{-4}$ in the limit $t \to \infty$, cancelling the $k$'s in the numerator and leaving an integral over $\vec{k}_1$ proportional to $\int d^3k_1 \left[\tilde{u}(k_1)\right]^2 \tilde{G}_{1\alpha}(k_1)$ .

When the $\mathcal{Q}_\alpha^\beta$ have been evaluated, equation 116 becomes our result for a general potential. As before, it is in the form of an integral over Fourier transform variables, and we must choose a particular potential in order to proceed further.

We can see that the qualitative behavior of $\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)}$ is what we would expect. For $t \to 0$, $\langle \vec{p}_1(0)\vec{p}_1(t)\rangle^{(2)}$ vanishes, and as $t \to \infty$ it approaches some function of $\beta, m_1, m_j, m_n$, the form of which is not yet clear.

We now consider the time integrals.

The evaluation of $\mathcal{Q}_2^\alpha$ is elementary, at least if we are willing to accept tabulated functions, but $\mathcal{Q}_1^\alpha$ and $\mathcal{Q}_3^\alpha$ require that we evaluate the integral

$$J_\alpha = \int_0^t e^{-G_\alpha^2 \tau_1^2} \int_0^{(E_\alpha + H_\alpha)\tau_1} e^{-x^2}\, dx\, d\tau_1 \,. \qquad (117)$$

Efforts to evaluate this for finite $t$ were unsuccessful, but it can be evaluated for $t \to \infty$ . We thus content ourselves with an expression for

$$\lim_{t\to\infty} \langle \vec{p}_1(0)\,\vec{p}_1(t) \rangle^{(2)} .$$

We use the series representation for the error function under the integral of $\mathcal{J}_\alpha$, letting $J_\alpha = E_\alpha + H_\alpha$:

$$\begin{aligned} \mathcal{J}_\alpha(t) &= J_\alpha \int_0^t e^{-G_\alpha^2 \tau_1^2}\, \tau_1 \left[ 1 - \frac{J_\alpha^2 \tau_1^2}{1!\,3} + \frac{J_\alpha^4 \tau_1^4}{2!\,5} - + \cdots \right] d\tau_1 \\ &= \sum_{n=0}^{\infty} \frac{J_\alpha^{2n+1} (-1)^n}{n!\,(2n+1)} \int_0^t \tau_1^{2n+1} e^{-G_\alpha^2 \tau_1^2} d\tau_1 \quad . \end{aligned} \tag{118}$$

In the limit $t \to \infty$ , the integral is a $\Gamma$ function, and

$$\lim_{t\to\infty} \mathcal{J}_\alpha(t) = \frac{1}{2G_\alpha} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{2n+1} , \tag{119}$$

where $z = J_\alpha / G_\alpha$.

This sum can be evaluated by a method of Wheelon (30). We observe that $1/(2p+1)$ is the Laplace transform of $\frac{1}{2} e^{-y/2}$ , and write:

$$\lim_{t\to\infty} \mathcal{J}_\alpha(t) = \frac{z}{4G_\alpha} \int_0^\infty dy\, e^{-y/2} \sum_{n=0}^{\infty} (-1)^n e^{-an} , \tag{120}$$

where $a = -2 \ln z + y$. This is a geometric sum, so

$$\mathcal{J}_\alpha(\infty) = \frac{z}{4G_\alpha} \int_0^\infty dy\, e^{-y/2} \frac{1}{1+e^{2\ln z - y}} \tag{121}$$

$$= \frac{L}{2G_\alpha} \int_0^\infty dx \frac{1}{L^2 e^x + e^{-x}} , \tag{122}$$

where $L = z^{-1}$.

Thus,

$$\mathcal{J}_\alpha(\infty) = \frac{L}{2G_\alpha} \int_1^\infty \frac{dw}{L^2 w^2 + 1} = \frac{z^2}{2G_\alpha} \left[ \frac{\pi}{2} - \tan^{-1} z \right] . \tag{123}$$

The series in equation 119 is divergent for $z > 1$. However, the right-hand side of equation 122 is an analytic function of $z$ for all $z$, so must hold as the correct value of $\mathcal{J}_\alpha(\infty)$ for all $z$ by analytic continuation.

Now that we have $\mathcal{J}_\alpha(\infty)$, we can obtain all the $\mathcal{Q}_\alpha^\beta(\infty)$ with some algebra and a few partial integrations. The result is

$$\mathcal{Q}_1^\alpha(\infty) = \frac{-(E_\alpha + F_\alpha/E_\alpha)}{4(D_\alpha^2 - F_\alpha^2/E_\alpha^2)^2} \frac{1}{\left[1 + \frac{(E_\alpha + F_\alpha/E_\alpha)^2}{(D_\alpha^2 - F_\alpha^2/E_\alpha^2)}\right]}$$

$$- \left[4\sqrt{D_\alpha^2 - F_\alpha^2/E_\alpha^2}\,(E_\alpha - F_\alpha/E_\alpha)^2\right]^{-1} \left[\frac{\pi}{2} - \tan^{-1}\left(\frac{\sqrt{D_\alpha^2 - F_\alpha^2/E_\alpha^2}}{E_\alpha + F_\alpha/E_\alpha}\right)\right] , \tag{124}$$

$$\mathcal{L}_2^{\alpha}(\infty) = \frac{1}{4(D_\alpha^2+2F_\alpha+E_\alpha^2)} \quad , \qquad (125)$$

$$\mathcal{L}_3^{\alpha}(\infty) = \frac{-(E_\alpha+F_\alpha/E_\alpha)}{4(D_\alpha^2-2F_\alpha+E_\alpha^2)} + \frac{\pi}{4\sqrt{D_\alpha^2-F_\alpha^2/E_\alpha^2}}$$
$$- \frac{(E_\alpha+F_\alpha/E_\alpha)^2}{(D_\alpha^2-F_\alpha^2/E_\alpha^2)^{3/2}}\left[\frac{\pi}{2}-\tan^{-1}\left(\frac{E_\alpha+F_\alpha/E_\alpha}{\sqrt{D_\alpha^2-F_\alpha^2/E_\alpha^2}}\right)\right]. \qquad (126)$$

Now that the $\mathcal{L}_\alpha^\beta$ have been evaluated for the limit $t \to \infty$ , equation 116 furnishes our desired general expression for $\langle \vec{p}_1(0)\, \vec{p}_1(\infty)\rangle^{(2)}$ . For our present purposes, it is not necessary to carry out the $\vec{k}$ integrations for a particular potential, nor is it necessary to proceed with further applications of the perturbation series, although there may be some of considerable interest.

## D. DISCUSSION

It must be admitted that the research reported in part III of this thesis enjoyed only a qualified success. First, the original intent was to create an approximation scheme for time-correlation functions which would be not only valid, but also directly useful, for ionic solutions, which are very dense systems.

The perturbation scheme here developed is formally valid for all systems for which the potentials are sums of pair potentials. Also, the assumption of convergence is not a drastic one. However, in the present simple form of the scheme, large numbers of terms must perhaps be taken for systems in which the potential energy is comparable to or larger than the kinetic energy, which is the case in a condensed system.

Still, there is currently considerable interest in rarefied systems such as plasmas, and the work of this part of the thesis is directly useful for these, and provides a considerable improvement over treatments which neglect entirely intermolecular forces, such as the work of Taylor on electric field autocorrelations in a plasma (22).

The work of Ron and Kalman (19a-c), based on the work of Gasiorowicz, Neuman, and Riddell (19d) is also capable of giving corrections to the zero-order approximation of time-dependent ensemble averages. However, their work, although very detailed, does not present a single, unified perturbation scheme. Rather, it is a sort of Taylor series expansion around an unperturbed path, followed by approximation of the expansion variable. This can be used for low orders, but becomes progressively clumsier for higher orders, and furnishes no general expressions.

The work of Prigogine's school (10) and of Andrews (11) is beyond the present understanding of this author, and furnishes, by its very complexity, impetus for such relatively simple-minded treatments as the preceding scheme.

The work of this part of the thesis may be considered as a beginning, and much more work and refinement can surely be spent with profit on this technique. For example, if infinite potentials, such as hard cores, are introduced, the Fourier transform of the potential diverges, and methods must be sought to overcome this (10b). Means of overcoming other divergences which can arise must also be sought. For example, the zero-order Fokker-Planck coefficient, which was calculated by Helfand, diverges for a coulomb potential, and the infinite part is presumably cancelled rigorously by higher-order terms, and a means of removing these divergences by partial summations analogous to those of part II of this thesis would seem to be a very worthwhile research objective. Helfand removed the divergence by introducing a finite upper limit in a Fourier transform integration, but this cutoff, although commonly used in plasma treatments, is arbitrary, and rigorous treatment avoiding this would of course be a considerable achievement.

The applications of the perturbation scheme to a Fokker-Planck coefficient and to a momentum autocorrelation function are illustrative of many other applications which could be made. In particular, it would be of interest to attempt treatment of a system having hard-core plus coulomb potentials.

The formal simplicity of our perturbation expansion would make it seem very worthwhile to seek extensions and further applications.

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# PROPOSITION I

It is proposed that the results of section I of this thesis be applied to a three-level maser, contradicting published work of Barker (1) and Scovil and Schulz-DuBois (2).

Equation 39 of part I of this thesis gives the entropy production for a system undergoing photochemical reactions under conditions of local equilibrium. It is:

$$\phi = \frac{1}{T_h} \sum_{k=1}^{t} A_k \frac{d\xi_k}{dt} + \rho\epsilon\left(\frac{1}{T_h} - \frac{1}{T_r}\right) \tag{1}$$

where $\phi$ is the entropy production, the $\xi$'s are progress variables in molecules per unit volume, $A_k$ is the negative of the free energy change per molecule of the reaction (the affinity), $T_h$ is the thermal temperature, $\rho$ is the density, $\epsilon$ is the rate per unit mass of energy absorption from the radiation, and $T_r$ is the radiation temperature.

We idealize a three-level maser as N identical particles, independent of each other, but interacting with the radiation field, and each able to occupy any one of three energy levels.

As does Barker, we will consider the systems in each state to be a separate "chemical species," $B_i$ (i=1, 2, 3), and transitions between levels to be "chemical reactions."

We consider six reactions

$$B_2 \rightleftharpoons B_1 \; ; \; A_1 = \mu_2 - \mu_1 \; ; \; d\xi_1 = d_1 n_1 = -d_1 n_2 \; ; \qquad \text{(I)}$$

$$B_3 \rightleftharpoons B_2 \; ; \; A_2 = \mu_3 - \mu_2 \; ; \; d\xi_1 = d_2 n_2 = -d_2 n_3 \; ; \qquad \text{(II)}$$

$$B_3 \rightleftharpoons B_1 \; ; \; A_3 = \mu_3 - \mu_1 \; ; \; d\xi_3 = d_3 n_1 = -d_3 n_3 \; ; \qquad \text{(III)}$$

$$B_3 \rightleftharpoons B_1 + h\nu_{31} \; ; \; A_4 = \mu_3 - \mu_1 \; ; \; d\xi_4 = d_4 n_1 = -d_4 n_3 \; ; \qquad \text{(IV)}$$

$$B_2 \rightleftharpoons B_1 + h\nu_{21} \; ; \; A_5 = \mu_2 - \mu_1 \; ; \; d\xi_5 = d_5 n_1 = -d_5 n_2 \; ; \qquad \text{(V)}$$

$$B_3 \rightleftharpoons B_2 + h\nu_{32} \; ; \; A_6 = \mu_3 - \mu_2 \; ; \; d\xi_6 = d_6 n_2 = -d_6 n_3 \, . \qquad \text{(VI)}$$

Here $h$ is Planck's constant the $\nu'$s are frequencies, and the $\mu'$s are chemical potentials.

We assume now that the part of the radiation field important for maser operation can be adequately represented by two radiation temperatures (not necessarily different), one for a narrow band of frequencies around $\nu_{32}$ and another for a narrow band around $\nu_{31}$ . In other parts of the spectrum, and perhaps in directions other than in certain small solid angles, the radiation temperature may be near $T_h$ . Equation 1 now becomes

$$\phi = \frac{1}{T_n}\sum_{k=1}^{6} A_k \frac{d\xi_k}{dt} - h\nu_{13}\frac{d\xi_4}{dt}\left(\frac{1}{T_n} - \frac{1}{T_{r_{13}}}\right) - h\nu_{12}\frac{d\xi_5}{dt}\left(\frac{1}{T_n} - \frac{1}{T_{r_{12}}}\right) - h\nu_{23}\frac{d\xi_6}{dt}\left(\frac{1}{T_n} - \frac{1}{T_{r_{23}}}\right). \tag{2}$$

In the operation of our system as a maser, an external source provides radiation at temperature $T_{r_{13}}$ in the narrow band around $\nu_{13}$, causing reaction IV to proceed to the left. A weak signal is introduced, causing reaction VI to proceed to the right by stimulated emission, giving a coherently amplified signal. The other reactions proceed in some manner.

We will now neglect spontaneous emission, as well as any emission or absorption outside of the small solid angles in which the pump and signal radiation is concentrated. Thus $\dot{\xi}_5 \approx 0$, and $\dot{\xi}_6$ and $\dot{\xi}_4$ are due only to stimulated emission and absorption.

A simple calculation shows that

$$\sum_{k=1}^{6} A_k \dot{\xi}_k \equiv 0 \tag{3}$$

for a steady state, which is the case Barker treats. However, he assumes that the only source of entropy production is from reactions I, II, and III, which is shown by equation 3 to be incorrect.

After writing

$$\sum_{k=1}^{3} A_k \dot{\xi}_k \qquad (4)$$

for the entropy production, Barker expresses the $\dot{\xi}$ in terms of transition probabilities and affinities, after assuming $h\nu \ll kT$ , $A \ll kT$ . Since he is treating the steady state, he minimizes $\phi$ with respect to $A_1$ , at constant $A_3$ (constant pump intensity). Although he is able to obtain a population expression which resembles one obtained from rate equations, his result can not be correct, since he does not use the correct entropy production.

Several attempts were made at obtaining a population expression by minimizing the correct entropy production expression, with the constraint $A_3$ = constant. Since the exact expression led to a complicated transcendental equation, various approximations were attempted, but no reasonable result was obtained. The probable cause for this is that the theorem requiring minimum entropy production for a steady state requires linear dependence of fluxes on forces for its derivation, and a maser certainly does not operate in the linear range if there is one. There may not be a linear range since it is not apparent how to express the term $\rho\epsilon(T_h^{-1} - T_r^{-1})$ in the form $LX^2$ .

We can obtain a useful piece of information from equation 2, using equation 3; the second law, $\phi \geq 0$ ;

and our assumption, $\dot{\xi}_5 \approx 0$ . We find

$$\frac{\nu_{13}\,\dot{\xi}_4\left(T_h^{-1} - T_{r_{13}}^{-1}\right)}{\nu_{23}\,\dot{\xi}_6\left(T_h^{-1} - T_{r_{23}}^{-1}\right)} \geq 1 \quad . \tag{5}$$

If we define the maser efficiency,

$$\eta_M \equiv \frac{\nu_{23}\,\dot{\xi}_6}{\nu_{13}\,\dot{\xi}_4} \quad , \tag{6}$$

we find from equation 5,

$$\eta_M \leq \frac{\dfrac{1}{T_h} - \dfrac{1}{T_{r_{13}}}}{\dfrac{1}{T_h} - \dfrac{1}{T_{r_{23}}}} \quad , \tag{7}$$

which is a ratio of Carnot limiting efficiencies. This differs from a result of Scovil and Schulz-DuBois, which is

$$\eta_M \leq T_h\left(\frac{1}{T_h} - \frac{1}{T_{r_{13}}}\right) \quad . \tag{8}$$

The numerical difference will generally be small, but it is apparent that their result would correspond to an infinite $T_r$ in the output signal, which is in principle unattainable.

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## PROPOSITION II

A derivation of a many-particle Fokker-Planck equation for the ions in an ionic solution is proposed. Kirkwood gives (1), without proof, a many-particle equation of this form, which is slightly different from the one we shall obtain.

Beginning with the N-particle Liouville equation, we integrate over the coordinates and momenta of all solvent molecules, and apply Green's theorem. The reduced distribution functions are those of part II (see equation II 4) but are now time-dependent. We obtain

$$\frac{\partial f^{(n)}}{\partial t} + \sum_{j=1}^{n} \left\{ \frac{\vec{p}_j}{m_j} \cdot \nabla_{r_j} f^{(n)} + \sum_{\substack{\ell=1 \\ \ell \neq j}}^{n} \nabla_{p_j} \cdot \vec{F}_{j\ell}\, f^{(n)} \right\} = \tag{1}$$

$$= - \sum_{j=1}^{n} \nabla_{p_j} \cdot \sum_{\ell=n+1}^{N} \int \cdots \int \vec{F}_{j\ell}\, f^{(N)}\, dP\, dR \quad .$$

We have assumed pairwise additivity of forces, and call $\vec{F}_{j\ell}$ the force on particle $j$ due to particle $\ell$. The set $\underset{\sim}{n}$ is the set of ions, and $\underset{\sim}{N}-\underset{\sim}{n}$ is the solvent, and we use $r, p$ and $R, P$ for their respective coordinates and momenta. We shall use $\mathcal{R}$ and $\mathcal{P}$ for the set $\underset{\sim}{N}$.

At this point, we introduce time-smoothing. This is the artifice that introduces irreversibility into the reversible Liouville equation. The time-smoothed distribution function is defined:

$$\bar{f}^{(\underset{\sim}{n})}(r,p;t) \equiv \frac{1}{\tau}\int_0^{\tau} f^{(\underset{\sim}{n})}(r,p;t+s)\,ds \quad . \tag{2}$$

After time-smoothing, equation 1 becomes

$$\frac{\partial \bar{f}^{(\underset{\sim}{n})}}{\partial t} + \sum_{j=1}^{\underset{\sim}{n}} \left\{ \frac{\vec{p}_j}{m_j} \cdot \nabla_{r_j} \bar{f}^{(\underset{\sim}{n})} + \sum_{\substack{\ell=1 \\ \ell \neq j}}^{\underset{\sim}{n}} \nabla_{p_j} \cdot \overline{\vec{F}_{j\ell}\, f}^{(\underset{\sim}{n})} \right\} = \sum_{j=1}^{\underset{\sim}{n}} \sum_{\ell=n+1}^{\underset{\sim}{N}} \Omega_{j\ell}^{(\underset{\sim}{n})} \; , \tag{3}$$

where

$$\Omega_{j\ell}^{(\underset{\sim}{n})} = -\frac{1}{\tau}\int_0^{\tau}\iint\cdots\int \vec{F}_{j\ell}(t+s)\, f^{(\underset{\sim}{N})}(t+s)\, dP\, dR\, ds \quad . \tag{4}$$

We shall use the method of Ross (2). His phase space transformation function is defined by:

$$f^{(\underset{\sim}{N})}(R,P;t+s) = \int\cdots\int K^{(\underset{\sim}{N})}(R,P\,|\,R_0,P_0;s)\, f^{(\underset{\sim}{N})}(R_0,P_0;t)\, dR_0\, dP_0 \, . \tag{5}$$

Equations 9 through 17 in Ross' article are directly applicable. Using our equation 5 to express $f^{(\underset{\sim}{N})}(t+s)$ , and Ross' equation 17, we find

$$\Omega_{j\ell}^{(\underset{\sim}{n})} \cong -\frac{1}{\tau}\int_0^{\tau}\int\cdots\int \vec{F}_{j\ell}(R_{j\ell}) \Big\{ \Big[ 1 - \sum_{k=1}^{N} \overrightarrow{\Delta P}_k^{(1)}(s) \cdot \nabla_{P_k} \Big] \times$$

$$\times \prod_{m=1}^{n} \delta(r_m - r_{m_0})\, \delta(p_m - p_{m_0})\, f^{(\underset{\sim}{N})}(R_0,P_0;t)\, dP_0\, dR_0\, dp_\ell\, dr_\ell\, dP\, dR\, ds. \tag{6}$$

where we now use $P$ and $R$ for the set $\underset{\sim}{N}-\underset{\sim}{n}-\ell$ .

Using Ross' equations 22 through 24, we have

$$f^{(\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t) \cong \left[1 + \sum_{k=1}^{\underset{\sim}{N}} \vec{\Delta p}_k^{(1)}(s) \cdot \nabla_{p_{k0}}\right] f^{(\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t+s) . \quad (7)$$

We shall discard all terms of higher order in $\vec{\Delta p}^{(1)}$ , those linear in $\vec{\Delta p}^{(2)}$ , etc., as we proceed. Ross discusses these approximations in his paper.

Now we rewrite $f^{(\underset{\sim}{N})}$, defining the correlation function, $\varphi_{\underset{\sim}{n}}^{(n)}$, and $f^{(\underset{\sim}{n}/\underset{\sim}{N})}$ , the conditional distribution function.

$$\begin{aligned} f^{(\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t+s) &= f^{(\underset{\sim}{n})}(p_0, r_0; t+s) f^{(\underset{\sim}{n}/\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t+s) \\ &= \varphi_{\underset{\sim}{n}}^{(n)}(p_0, r_0; t+s)\left[\prod_{i=1}^{\underset{\sim}{n}} f_i^{(1)}(r_{i0}\, p_{i0}; t+s)\right] f^{(\underset{\sim}{n}/\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t+s) . \end{aligned} \quad (8)$$

We shall require this written for the set $\underset{\sim}{n}+\ell$ instead of for $\underset{\sim}{n}$ .

With Ross, we assume that the $f^{(1)}$'s acted on by the $\nabla_{p_{k0}}$ and the $\varphi_{\underset{\sim}{n}+\ell}^{(n+1)}$ can be replaced by the equilibrium functions. Thus

$$\nabla_{p_{k0}} f_k^{(1)}(r_{k0}, p_{k0}) = -\beta \frac{\vec{p}_{k0}}{m_k} f^{(1)}(r_{k0}, p_{k0}) , \quad (9)$$

and equation 7 becomes

$$f^{(\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t) = \left[1 - \sum_{k=1}^{\underset{\sim}{n}+\ell} \vec{\Delta p}^{(1)}(s) \cdot \beta \frac{\vec{p}_{k0}}{m_k}\right] f^{(\underset{\sim}{N})}(\mathcal{P}_0, \mathcal{R}_0; t+s) . \quad (10)$$

We now obtain the following expression for $\Omega_{j\ell}^{(\underline{n})}$ :

$$\begin{aligned}\Omega_{j\ell}^{(\underline{n})} &= -\frac{1}{\tau}\int_0^\tau\int\cdots\int \vec{F}_{j\ell}(r_j,r_\ell)\Big\{\Big[1-\sum_{i=1}^{N}\vec{\Delta p}_i^{(1)}(s)\cdot\nabla_{p_i}\Big]\prod_{m=1}^{\underline{n}}\delta(r_m-r_{m_0})\,\delta(p_m-p_{m_0})\;\times\\ &\times\Big[1-\beta\sum_{k=1}^{\underline{n}+\ell}\Delta p_k^{(1)}(s)\cdot\frac{\vec{p}_{k_0}}{m_k}\Big]f^{(\underline{N})}(R_0,P_0;t+s)\,dP_0\,dR_0\,dp_\ell\,dr_\ell\,dP\,dR\,ds\\ &= -\frac{1}{\tau}\int_0^\tau\int\cdots\int \vec{F}_{j\ell}(r_{j_0},r_\ell)\Big[1-\sum_{i=1}^{N}\Delta p_i^{(1)}(s)\cdot\nabla_{p_i}\Big]\Big[1-\beta\sum_{k=1}^{\underline{n}+\ell}\vec{\Delta p}_k^{(1)}(s)\cdot\frac{p_k}{m_k}\Big]\;\times\\ &\times\exp\Big\{-\beta W_{\underline{n}+\ell}^{(n+1)}(r_1\cdots r_\ell)\Big\}\prod_{q=1}^{\underline{n}+\ell}f_q^{(1)}(t+s)\;{}^{\circ}f^{(\underline{n}+\ell/\underline{N})}(P,R;t+s)\,dp_\ell\,dr_\ell\,dP\,dR\,ds\,.\end{aligned}\tag{11}$$

Only the terms for $i$ in the set $\underline{n}$ will survive in the $i$ sum. Note that in equation 11, $\varphi_{\underline{n}+\ell}^{(n+1)}$ has been approximated by the equilibrium function, ${}^{\circ}\varphi_{\underline{n}+\ell}^{(n+1)} = \exp\{-\beta W_{\underline{n}+\ell}^{n+1}\}$ . $W^{(n+1)}$ is a potential of mean force, defined as in part II of the thesis.

We drop terms of $O([\Delta p^{(1)}]^2)$ ,and from equation 3 we obtain

$$\begin{aligned}&\frac{\partial\bar{f}^{(\underline{n})}}{\partial t}+\sum_{j=1}^{\underline{n}}\Big\{\frac{\bar{p}_j}{m_j}\cdot\nabla_{r_j}\bar{f}^{(\underline{n})}+\sum_{\substack{\ell=1\\ \ell\neq j}}^{\underline{n}}\nabla_{p_j}\cdot\bar{F}_{j\ell}\bar{f}^{(n)}\Big\}=\\ &=\sum_{j=1}^{\underline{n}}\nabla_{p_j}\cdot\sum_{\ell=n+1}^{N}\Big[-\frac{1}{\tau}\int_0^\tau\int\cdots\int F_{j\ell}(r_{j_0},r_\ell)f^{(\underline{N})}(P,R;t+s)\,ds\,dp_\ell\,dr_\ell\,dP\,dR\\ &+\frac{1}{\tau}\int_0^\tau\int_0^s\int\cdots\int\vec{F}_{j\ell}(r_{j_0},r_\ell)\sum_{i=1}^{\underline{n}}\vec{F}_i\Big(R_0+s'\frac{P_0}{m}\Big)\cdot\nabla_{p_i}f^{(n)}(p,r;t+s)f^{(\underline{n}/N)}(P,R;t+s)\,dp_\ell\,dr_\ell\,dP\,dR\,ds'\,ds\\ &+\frac{\beta}{\tau}\int_0^\tau\int_0^s\int\cdots\int\vec{F}_{j\ell}(r_{j_0},r_\ell)\sum_{i=1}^{\underline{n}}\vec{F}_i\Big(R_0+s'\frac{P_0}{m}\Big)\cdot\frac{\vec{p}_i}{m_i}f^{(n)}(p,r;t+s)f^{(\underline{n}/N)}(P,R;t+s)\,dp_\ell\,dr_\ell\,dP\,dR\,ds'\,ds\\ &-\frac{\beta}{\tau}\int_0^\tau\int_0^s\int\cdots\int\vec{F}_{\ell j}(r_\ell,r_{j_0})\vec{F}_\ell\Big(R_0+s'\frac{P_0}{m}\Big)\cdot\frac{\vec{p}_\ell}{m_\ell}f^{(\underline{n}+\ell)}(p_\ell r_\ell PR;t+s)f^{(n+\ell/N)}(P,R;t+s)\,dp_\ell\,dr_\ell\,dP\,dR\,ds'\,ds\,.\end{aligned}\tag{12}$$

Making the standard assumptions concerning Plateau values in the time correlation function's integrals, we find after again time-smoothing:

$$\frac{\partial \bar{f}^{(\underline{n})}}{\partial t} + \frac{\vec{p}}{m}\cdot\nabla_r \bar{f}^{(\underline{n})} + \nabla_p\cdot\vec{F}_n^{\,*} f^{(n)} = \tag{13}$$

$$= \nabla_p\cdot\zeta_{\underset{\sim}{n}}^{(n)}\cdot\left\{\frac{\vec{p}}{m}\bar{f}^{(\underline{n})} + \frac{1}{\beta}\nabla_p\bar{f}^{(\underline{n})}\right\} .$$

Here we use the same vector notation in phase space as Kirkwood, and equation 13 is the same as his result (reference (1), equation 60) except for the definitions of some quantities in it. We define

$$\vec{F}_{\underset{\sim}{n}}^{\,*} = {}^{\underline{n}}\langle\vec{F}_{\underline{n}}\rangle^{\circ} + \sum_{\ell=n+1}^{N}\int\zeta_\ell^{(\underline{n})}\cdot\frac{\vec{p}_\ell}{m_\ell} f_\ell^{(1)}(p_\ell,r_\ell;t+s)\,dr_\ell\,dp_\ell + \vec{F}_{\underline{n}}^{\,+} , \tag{14}$$

where $F_{\underset{\sim}{n}}^{+}$ is a correction term to absorb all the approximations made, and is hopefully small,

$$\zeta_\ell^{(\underline{n})} = \sum_{j=1}^{n}\frac{\beta}{2}\int_{-\tau_n}^{\tau_n} {}^{\underline{n}+\ell}\langle\vec{F}_{\ell_j}\vec{F}(R+s\frac{p}{m})\rangle^{\circ}\,ds\,\exp\left\{-\beta\left[W^{\underline{n}+\ell}-W^{\underline{n}}\right]\right\}, \tag{15}$$

and

$$\zeta_{\underline{n}}^{(n)} = \sum_{j=1}^{n}\sum_{i=1}^{n}\frac{\beta}{2}\int_{-\tau_n}^{\tau_n} {}^{n}\langle\vec{F}_j'(R)\,\vec{F}_i(R+s\frac{p}{m})\rangle^{\circ}\,ds \quad , \tag{16}$$

where $\vec{F}_j{}' = \sum_{\ell=n+1}^{N} \vec{F}_{j\ell}$ .

We use the notation of Kirkwood. A left superscript on an ensemble average indicates particles not averaged over, and a right super zero means an equilibrium average. Note that equations 15 and 16 differ from Kirkwoods definitions. Kirkwood's $\zeta_{\ell}^{(n)}$ has no $W^{(n)}$ in it, and his $\zeta_{\underset{\sim}{n}}^{(n)}$ has only $i=j$ terms in it and has $\vec{F}_i{}'$ for the second $\vec{F}_i$ . In addition, of course, we have $\vec{F}_i(\mathcal{R}+s\frac{\mathcal{P}}{m})$ instead of $exp(-isL)\vec{F}_i(-\mathcal{R})$, as does Ross in his one-body equation.

Up to this point, our results apply, within the approximations made, to any system. Our particular application in which $\underset{\sim}{n}$ is the set of ions in a solution, is no different from the case of uncharged species only, since all of coordinates of the particles interacting with long range forces have been left unintegrated.

Note that at this point, we can, if we wish, insert the well-known approximation for ${}^{n}\langle \vec{F}_{\underset{\sim}{n}} \rangle^{\circ}$ given by $-\nabla_r \sum_{i<j}^{n} z_i z_j \epsilon^2 / (D|r_i - r_j|)$ .

Beginning with equation 13, we can now proceed to integrate over the coordinates and momenta of part of the ions, say all but the set $\underset{\sim}{m}$ , where $m \ll n$ . Either by a considerable amount of manipulation or by recognizing that the derivation of equation 13 is formally acceptable for long-range forces, we obtain an equation identical with equation 13 except that $\underset{\sim}{n}$ is replaced by $\underset{\sim}{m}$.

However, when we write equation 13 for the set $\underset{\sim}{m}$, we must use the proper cluster expansions for the ensemble averages in $\vec{F}_n^{\,*}$, $\zeta_\ell^{(\underline{n})}$, and $\zeta_{\underline{n}}^{(n)}$, since these quantities are sums of formally divergent terms, as discussed in part II of this thesis. ${}^{\underset{\sim}{m}}\langle \vec{F}_m \rangle^\circ$ poses no problem not treated in part II, nor do the potentials of mean force in $\zeta_\ell^{(\underline{n})}$. However, the time correlation functions, although evaluated to a linear trajectory approximation in the Ross theory, involve all particles, and must be treated in a different way.

## REFERENCES

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# PROPOSITION III

An alternative perturbation scheme for time-correlation functions, based on a method of von Roos (1), is proposed.

A formal solution of Liouville's equation has been published (1). However, this result, which is a series of scattering-type operators operating on a distribution function, cannot be applied directly to calculations of time-correlation functions*, so we derive a result that can be.

Von Roos uses a phase space transformation function similar to that of Ross (2). The only difference is that the $G^{(N)}(\mathcal{R},\mathcal{V},t\,|\,\mathcal{R}_0,\mathcal{V}_0,t_0)$ of von Roos is the retarded Green's function for the Liouville equation, while the $K^{(N)}(\mathcal{R},\mathcal{P};t\,|\,\mathcal{R}_0,\mathcal{P}_0;t_0)$ of Ross satisfies the Liouville equation. Thus, for times later than the initial time, the two functions are essentially identical.

We define a time-displaced distribution function, $g^{(N)}$:

$$g^{(N)}(\mathcal{R},\mathcal{P};t\,|\,\mathcal{R}_0,\mathcal{P}_0;t_0)=K^{(N)}(\mathcal{R},\mathcal{P};t\,|\,\mathcal{R}_0,\mathcal{P}_0;t_0)\,f^{(N)}(\mathcal{R}_0,\mathcal{P}_0;t_0)\ . \tag{1}$$

Since $K^{(N)}$ is the probability density that the system phase point be at $\mathcal{R},\mathcal{P}$ at time $t$ if it was known to be at $\mathcal{R}_0,\mathcal{P}_0$ at time $t_0$, $g^{(N)}$ is the joint probability

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* See p. 107 of this thesis.

that the pair of points be observed to be the location of the phase point at the pair of times. We could also use $G^{(N)}$ instead of $K^{(N)}$, arbitrarily introducing asymmetry in time at this point, but otherwise changing nothing.

Equation 1 can be integrated over the coordinates of $N-2$ particles at each time, giving

$$g^{(2)}(r,p,t|r_0,p_0,t_0)=K^{(2)}(r,p,t|r_0,p_0,t_0)f^{(2)}(r_0,p_0,t_0), \quad (2)$$

where $K^{(2)}$ is the reduced function of Rice and Allnatt (3).

We can go through an analysis of the von Roos type for $g^{(n)}$, but we work directly with $\langle\beta(r_0,p_0)\alpha(r,p)\rangle$ as follows:

$$\langle\beta(t_0)\alpha(t)\rangle=\int\beta(r_0,v_0)\alpha(r,v)G^{(N)}f^{(N)}(R_0,V_0,t_0)\,dR\,dV\,dR_0\,dV_0, \quad (3)$$

where we use the $G^{(N)}$ of von Roos.

In the case: $\beta = \delta(r_0-r_0')\delta(v_0-v_0')$
$\alpha = \delta(r-r')\delta(v-v')$,

$$\langle\beta(t_0)\alpha(t)\rangle = g^{(n)}(r',v',t|r_0',v_0',t_0), \quad (4)$$

so the analysis of $g^{(n)}$ is included as a special case of the analysis of $\langle\beta(t_0)\alpha(t)\rangle$. Of course, any $\langle\beta(t_0)\alpha(t)\rangle$ can be obtained with $g^{(n)}$, since

$$\langle \beta(t_0)\alpha(t)\rangle = \int \beta(r_0,v_0)\,\alpha(r,v)\,g^{(n)}(r,v,t) r_0,v_0,t_0)\,dr\,dv\,dr_0\,dv_0 \,. \tag{5}$$

Now we can use the expansion of $G^{(N)}$ given by von Roos (his #8 and 11 ) directly, except that we notice that his Liouville equation should have $\vec{F}\cdot\nabla_p = \frac{\vec{F}\cdot\nabla_v}{m}$ instead of $\vec{F}\cdot\nabla_v$ on the right-hand side. We correct this minor error in the following, using

$$\frac{\vec{F}\cdot\nabla_v}{m} = \frac{\vec{F}_1\cdot\nabla_{v_1}}{m_1} + \frac{\vec{F}_2\cdot\nabla_{v_2}}{m_2} + \cdots + \frac{\vec{F}_N\cdot\nabla_{v_N}}{m_N} \,.$$

The zeroth order term is:

$$\langle \beta(t_0)\alpha(t)\rangle^{(0)} = \int \beta(r_0,v_0)\,\alpha(r,v)\,\delta(V-V_0)\,\delta[R-R_0-V_0(t-t_0)]\times \\ \times\,\delta(t-t_0)\,f^{(N)}(R_0,V_0,t_0)\,dR\,dV\,dR_0\,dV_0 \tag{6}$$

$$= \int \beta(r_0,v_0)\,\alpha(r,v)\,\delta(v-v_0)\,\delta[r-r_0-v_0(t-t_0)]\,\delta(t-t_0)\,\times \\ \times\, f^{(m)}(r_0,v_0,t_0)\,f^{(m/N)}[r_0,v_0,R-V(t-t_0),V,t_0]\,dR\,dV\,dr_0\,dv_0 \,. \tag{7}$$

Now change integration variables to $r_0, v_0, r, v, R-V(t-t_0), V$. The Jacobian for this transformation is a triangular determinant with unit diagonal elements, so is unity.

Now:

$$\langle \beta(t_0)\alpha(t)\rangle = \int \beta(r_0,v_0)\,\alpha(r,v)\,\delta(v-v_0)\,\delta[r-r_0-v_0(t-t_0)]\,S(t-t_0)\,X$$

$$X\, f^{(n)}(r_0 v_0 t_0)\,dr\,dv\,dr_0\,dv_0\,dV\,d[R-V(t-t_0)] \qquad (8)$$

$$= \int \beta(r_0,v_0)\,\alpha(r_0+v_0(t-t_0))\,f^{(n)}(r_0,v_0,t_0)\,dr_0\,dv_0\,,$$

which is of course the rectilinear approximation.

Now we look at the nth term:

$$\langle \beta(t_0)\alpha(t)\rangle^{(n)} = (-1)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \int \beta(r_0,v_0)\,\alpha(r,v)\,X$$

$$X\, d\mathcal{R}\,d\mathcal{R}_0\,d\mathcal{V}\,d\mathcal{V}_0\,d\mathcal{V}_2 \cdots d\mathcal{V}_n\ X$$

$$X\ \delta\Big[\mathcal{R}-\mathcal{R}_0-\mathcal{V}(t-t_1)-\sum_2^n \mathcal{V}_j(t_{j-1}-t_j)-\mathcal{V}_0(t_n-t_0)\Big]\ X$$

$$X\ \frac{\vec{F}[\mathcal{R}-\mathcal{V}(t-t_1)]}{m}\cdot\nabla_{\mathcal{V}}\,\delta(\mathcal{V}-\mathcal{V}_2)\,\frac{F[\mathcal{R}-\mathcal{V}(t-t_1)-\mathcal{V}_2(t_1-t_2)]}{m}\cdot \qquad (9)$$

$$\cdot\nabla_{\mathcal{V}_2}\,\delta(\mathcal{V}_2-\mathcal{V}_3)\ \cdots\cdots\ \frac{\vec{F}[\mathcal{R}-\mathcal{V}(t-t_1)-\sum_2^n \mathcal{V}_j(t_{j-1}-t_j)-\mathcal{V}_0(t_n-t_0)]}{m}\cdot$$

$$\cdot\nabla_{\mathcal{V}_n}\,\delta(\mathcal{V}_n-\mathcal{V}_0)\,f^{(N)}(\mathcal{R}_0,\mathcal{V}_0,t_0)\ .$$

Here the $\mathcal{R}_1, \cdots, \mathcal{R}_n$ and $\mathcal{V}_1$ integrations have been performed.

Integration over $\mathcal{R}_0$ replaces $\mathcal{R}_0$ by

$$\mathcal{R}-\mathcal{V}(t-t_1)-\sum_2^n \mathcal{V}_j(t_{j-1}-t_j)-\mathcal{V}_0(t_n-t_0)$$

in $f^{(N)}$ and $r_0$ by

$$r - v(t-t_1) - \sum_2^n v_j\,(t_{j-1} - t_j) - v_0\,(t_n - t_0)$$

in $\beta$. We replace $\nabla_{\mathcal{V}_n}\delta(\mathcal{V}_n - \mathcal{V}_0)$ by $-\nabla_{\mathcal{V}_0}\delta(\mathcal{V}_n - \mathcal{V}_0)$ , etc., and then integration over $\mathcal{V}_0$ gives:

$$\begin{aligned}
\langle \beta(t_0)\alpha(t)\rangle^{(n)} = &-\int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n \int d\mathcal{R}\, d\mathcal{V}\, d\mathcal{V}_2 \cdots d\mathcal{V}_n \times \\
&\times \alpha(r,v)\, \frac{\vec{F}[\mathcal{R}-\mathcal{V}(t-t_1)]}{m} \cdot \nabla_{\mathcal{V}_2}\delta(\mathcal{V}-\mathcal{V}_2) \cdots \\
&\times \frac{\vec{F}[\mathcal{R}-\mathcal{V}(t-t_1)-\sum_2^n \mathcal{V}_j(t_{j-1}-t_j)]}{m} \cdot \\
&\cdot \Big(\nabla_{\mathcal{V}_0}\Big\{\beta[r-v(t-t_1)-\sum_2^n v_j(t_{j-1}-t_j)-v_0(t_n-t_0), v_0] \times \\
&\times f^{(N)}[\mathcal{R}-\mathcal{V}(t-t_1)-\sum_2^n \mathcal{V}_j(t_{j-1}-t_j)-\mathcal{V}_0(t_n-t_0), \mathcal{V}_0, t_0]\Big\}\Big)_{\mathcal{V}_0=\mathcal{V}_n}.
\end{aligned} \tag{10}$$

We rewrite the expression in the manner of von Roos, using operators that operate only on the first or second argument of $\beta$ or of $f^{(N)}$ instead of on the $\mathcal{V}_0$ variables. Now $\nabla_{\mathcal{V}_0}$ is replaced by $\nabla_v - (t_n-t_0)\nabla_r + \nabla_{\mathcal{V}} - (t_n-t_0)\nabla_{\mathcal{R}}$ where these operate only as follows: The first term operates on the second argument of $\beta$ , the second on the first argument of $\beta$ , the third on the second argument of $f^{(N)}$ and the last on the first argument of $f^{(N)}$ .

Further integrations over the $\mathcal{V}_j$ variables give the final result,

$$\langle \beta(t_0)\alpha(t)\rangle^{(n)} = (-1)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \int d\mathcal{R}\, d\mathcal{V}\, \alpha(r,v) \times$$

$$\times \prod_{\alpha=1}^{n} \left\{ \frac{\vec{F}[\mathcal{R}-\mathcal{V}(t-t_\alpha)]}{m} \cdot P_\alpha \right\} \left\{ \beta[r-v(t-t_0), v] \times \right.$$

$$\left. \times\, f^{(N)}[\mathcal{R}-\mathcal{V}(t-t_0), \mathcal{V}, t_0] \right\} \qquad (11)$$

where $P_\alpha = \nabla_{\mathcal{V}} - (t_\alpha - t_0)\nabla_{\mathcal{R}} + \nabla_v - (t_\alpha - t_0)\nabla_r - \sum_{\beta=\alpha+1}^{n} (t_\alpha - t_\beta)\nabla_{\mathcal{R}}$ .

In $P_\alpha$ , the first four operators operate only as before, and each $\nabla_{\mathcal{R}}$ in the sum operates on the argument of the $\frac{1}{m}\vec{F}[\mathcal{R}-\mathcal{V}(t-t_\gamma)]$, only if $\gamma = \beta$ . This is like the work of von Roos except for the presence of the $\beta$ , so we can use diagrams like his and reinterpret the line to the exterior vertex to represent the first four terms of our $P_\alpha$ . Equation 11 will be represented by $n!$ diagrams.

The integration over $\mathcal{R}$ and $\mathcal{V}$ must still be done in equation 11. This is inconvenient in the form shown, so we seek another way of writing it, to avoid the gradients operating on the distribution function.

Consider one term of equation 11, say the one represented by the diagram

(12)

with $\ell$ $(\ell \leq n)$ lines to the external vertex. We leave the terms of operators operating on $\beta$ unchanged and look at the $2^{\ell}$ terms composed of products of $\nabla_{v}$'s and $\nabla_{\mathcal{R}}$'s operating on $f^{(N)}$. Say there are $b$ $\nabla_{v}$'s and $\ell - b$ $\nabla_{\mathcal{R}}$'s in the product of $\ell$ $\nabla$'s.

Now we change from $\mathcal{R}, v$ variables to $\mathcal{R}', v$, where $\mathcal{R}' = \mathcal{R} - v(t-t_0)$. The Jacobian is unity, and since the $\nabla_{\mathcal{R}}$'s are simply a way of writing part of the $\nabla_{v}$'s, they are replaced by $\nabla_{\mathcal{R}'}$'s.

The term we are considering now becomes:

$$(-1)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \int d\mathcal{R}\, dv\, \alpha[r' + v(t-t_0), v]\, \beta[r', v] \times$$

$$\times \prod_{\alpha}{}' \left\{ \frac{\vec{F}[\mathcal{R}' + v(t_\alpha - t_0)]}{m} \cdot P_{\alpha \gamma_\alpha} \right\} \prod_{\beta}{}'' \left\{ \frac{\vec{F}[\mathcal{R}' + v(t_\beta - t_0)]}{m} \cdot \nabla_{\gamma} \right\} \times \tag{13}$$

$$\times \prod_{\lambda}{}''' \left\{ \frac{\vec{F}[\mathcal{R}' + v(t_\lambda - t_0)]}{m} \cdot (-t_\lambda + t_0) \nabla_{\mathcal{R}'} \right\} f^{(N)}(\mathcal{R}', v, t_0),$$

where we use $\prod'$ to include the vertices from which an internal line begins ( $n-\ell$ of these), $\prod''$ to include the $b$ $\nabla_v$'s and $\prod'''$ to include $\ell-b$ $\nabla_{\mathcal{R}'}$'s .

Now we apply Green's theorem $b$ times to the $v$ integration and $\ell-b$ times to the $\mathcal{R}'$ integration and obtain (assuming the surface integral vanishes):

$$(-1)^{n-b}\prod_{\lambda}{}''(t_\lambda-t_0)\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{n-1}}dt_n\,(\nabla_v\cdot)^b(\nabla_{\mathcal{R}'}\cdot)^{\ell-b}\times$$

$$\times\Big\{\alpha[r'+v(t-t_0), v]\,\beta[r',v]\prod_{\alpha}{}'\left(\frac{\vec{F}[\mathcal{R}'+v(t_\alpha-t_0)]}{m}\cdot P_{\alpha\gamma_\alpha}\right)\times$$

$$\times\prod_{\beta}{}^{\ell}\left(\frac{\vec{F}[\mathcal{R}'+v(t_\beta-t_0)]}{m}\right)\Big\}f^{(N)}\,d\mathcal{R}'\,dv \qquad (14)$$

where $\prod^{\ell}$ is $\prod''\times\prod'''$ . The divergences operate on the entire factor to their right, which is a cartesian tensor with $\ell$ free indices (of the lth rank). The $(\nabla\cdot)^{\alpha}$ notation is interpreted so that by $(\nabla\cdot)^2$ we mean $\nabla\nabla:$ , etc.

This is now an ensemble average of a function of only one set of coordinates and momenta.

# REFERENCES

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# PROPOSITION IV

An approximate solution for the temperature distribution in a reaction vessel immersed in a constant-temperature bath is proposed.

It is known (1) that temperature gradients in reaction vessels can be appreciable for cases in which no mixing occurs. In cases for which convection is negligible, the temperature distribution very nearly obeys the equation (2):

$$\frac{\partial T}{\partial t} = \frac{K}{\rho c} \nabla^2 T + \frac{\mathcal{R} H}{\rho c} \quad . \tag{1}$$

Here $T$ is the temperature, $K$ is the coefficient of thermal conductivity, $\mathcal{R}$ is the specific reaction rate, $H$ is the heat of reaction, $\rho$ is the density, and $c$ is the heat capacity.

Benson (1) has published a solution for equation 1 based on the assumption that $\mathcal{R}$, $H$, $\rho$, $c$, and $K$ are constants. Wilson (2) has published a steady-state solution (setting $\partial T/\partial t = 0$) for the case in which

$$\begin{aligned} \mathcal{R} &\cong A \exp(-E^{\dagger}/RT) \left[1 + \frac{E^{\dagger}\tau}{RT_0}\right] \\ &\cong \mathcal{R}_0 \left[1 + E^{\dagger}\tau / RT_0^2\right] \quad , \end{aligned} \tag{2}$$

where $E^{\dagger}$ is the Arrhenius activation energy, $A$ is a constant, $\tau \equiv T - T_0$, $T_0$ is the wall temperature, and $R$ is the gas constant.

We consider the case of a spherical reaction vessel of radius $r_0$. Equation 1 becomes

$$\frac{\partial \tau}{\partial t} = \frac{K}{\rho c} \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\tau) + \frac{\mathcal{R} H}{\rho c} \quad . \tag{3}$$

Benson's work corresponds to a solution of equation 3 with $\mathcal{R}$ replaced by $\mathcal{R}_0$. We attempt an approximate solution using equation 2 for $\mathcal{R}$.

Benson's solution is:

$$\tau_B = \frac{\mathcal{R}_0 H r_0^2}{6K}\left[1 - \frac{r^2}{r_0^2} + \frac{12 r_0}{\pi^3 r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} \sin\left(\frac{\pi n r}{r_0}\right) e^{-\frac{n^2 \pi^2 K t}{r_0^2 \rho c}}\right]$$

$$= \frac{\mathcal{R}_0 H r_0^2}{6K}\left[1 - \frac{r^2}{r_0^2} + \frac{1}{r}\sum_{n=1}^{\infty} \psi_n\right] \quad , \tag{4}$$

We let $r\tau = \varphi$, and equation 3 becomes, using equation 2:

$$\frac{\partial \varphi}{\partial t} = \frac{K}{\rho c} \frac{\partial^2}{\partial r^2}\varphi + \frac{\mathcal{R}_0 H r}{\rho c} + \frac{\mathcal{R}_0 H E^{\dagger}}{\rho c R T_0^2}\varphi \quad . \tag{5}$$

We assume, with Benson, that the reaction is sufficiently slow that $\mathcal{R}_0$ does not vary appreciably with time or position in the cell.

Since the $\psi_n$ are a complete set of functions, at least for functions having the right symmetry and obeying the right boundary conditions, we attempt a solution in the form

$$\varphi = \frac{\mathcal{R}_0 H r_0^2}{6K}\left[ r - \frac{r^3}{r_0^2} + \sum_{n=1}^{\infty} b_n(t)\, \psi_n \right] . \qquad (6)$$

We write

$$\frac{\partial \varphi}{\partial t} = \left(\frac{\partial \varphi}{\partial t}\right)_b + \frac{\mathcal{R}_0 H r_0^2}{6K} \sum_{n=1}^{\infty} \frac{\partial b_n(t)}{\partial t} \psi_n , \qquad (7)$$

where $(\partial\varphi/\partial t)_b$ is the derivative with respect to time if $b_n$ were a constant.

Putting equation 7 into equation 5, we find

$$\left(\frac{\partial \varphi}{\partial t}\right)_b + \frac{\mathcal{R}_0 H r_0^2}{6K} \sum_{n=1}^{\infty} \frac{\partial b_n}{\partial t} \psi_n = \frac{K}{\rho c} \frac{\partial^2}{\partial r^2} \varphi + \frac{\mathcal{R}_0 H r}{\rho c} + \frac{\mathcal{R}_0 H E^+}{\rho c R T_0^2} \varphi , \qquad (8)$$

But

$$\left(\frac{\partial \varphi}{\partial t}\right)_b = \frac{K}{\rho c} \frac{\partial^2}{\partial r^2} \varphi + \frac{\mathcal{R}_0 H r}{\rho c} , \qquad (9)$$

so

$$\frac{\mathcal{R}_0 H r_0^2}{6K} \sum_{n=1}^{\infty} \frac{\partial b_n}{\partial t} \psi_n = \frac{\mathcal{R}_0 H E^+}{\rho c R T_0^2} \varphi . \qquad (10)$$

Now we multiply equation 10 by $\psi_m$ and integrate over $r$ from $0$ to $r_0$. We obtain,

$$\frac{\mathcal{R}_0 H r_0^2}{6K} \frac{\partial b_m}{\partial t} \int_0^{r_0} \psi_m^2 dr = \frac{\mathcal{R}_0^2 H^2 r_0^2 E^+}{6K \rho c R T_0^2} \left[ \int_0^{r_0} \left(r - \frac{r^3}{r_0}\right) \psi_m dr + b_m \int_0^{r_0} \psi_m^2 dr \right],$$

due to the orthogonality of the $\varphi_m$ .

After doing the integrations and performing some manipulations, we obtain

$$\frac{\partial b_m}{\partial t} = \frac{\mathcal{R}_0 H E^+}{\rho c R T_0^2}\left[\exp\left\{\frac{m^2 K t}{r_0^2 \rho c}\right\} + b_m\right] . \tag{12}$$

The solution of equation 12 is:

$$b_m(t) = \exp\left\{\frac{\mathcal{R}_0 H E^+ t}{\rho c R T_0^2}\right\} + \frac{\mathcal{R}_0 H E^+ / \rho c R T_0^2}{\frac{m^2 K}{r_0^2 \rho c} - \frac{\mathcal{R}_0 H E^+}{\rho c R T_0^2}} \exp\left\{\frac{m^2 K t}{r_0^2 \rho c}\right\} . \tag{13}$$

Our solution is now:

$$\tau = \frac{\varphi}{r} = \frac{\mathcal{R}_0 H r_0^2}{6K}\left[1 - \frac{r^2}{r_0^2} + \frac{12 r_0}{\pi^3 r}\sum_{n=1}^{\infty} b_n \frac{(-1)^n}{n^3} \sin\left(\frac{\pi n r}{r_0}\right) e^{-\frac{n^2 \pi^2 K t}{r_0^2 \rho c}}\right], \tag{14}$$

where $b_n$ is given by equation 13.

We notice that, in order for the solution not to diverge in the limit $t \to \infty$ , we must require

$$\frac{\mathcal{R}_0 H E^+}{\rho c R T_0^2} < \frac{\pi^2 K t}{r_0^2 \rho c} . \tag{15}$$

This is not surprising, since our treatment is limited anyway to slow reactions.

For the following values of the parameters:

$$\begin{aligned} E^{+} &= 20 \text{ kcal mole}^{-1} \\ T_0 &= 300 \text{ deg K} \\ \rho c &= 1 \text{ cal cm}^{-3} \text{deg}^{-1} \\ K &= 1 \times 10^{-3} \text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1} \\ r_0 &= 5 \text{ cm} \end{aligned} \qquad (16)$$

we find that $\mathcal{R}_0$ must be smaller than about $2 \times 10^{-4}$ mole liter$^{-1}$ second$^{-1}$. This is fairly slow, but there are reactions of interest that proceed this slowly.

Now that we have the temperature distribution, we can, in principle, integrate a given temperature-dependent rate equation, but this is likely to be impossible without a high-speed computer.

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## PROPOSITION V

A modification is proposed of the model of Saunders and Ross(1) for the reaction between polyadenylic acid and polyuridylic acid.

This reaction, which forms a two-stranded helix, is found to exhibit a decreasing rate with increasing temperature. The model of Saunders and Ross proposes a series of steps, each having ordinary temperature-dependence, and each adding one more cross-link to the double chain, and is able to fit experimental data reasonably well, although using more than one free parameter to do so.

The rate of the initiation reaction is assumed to follow:

$$v_0 = k_0 AB - k_\mu C_1 \tag{1}$$

where $v_0$ is the rate, $k_0$ is the forward rate constant, $A$ and $B$ are the concentrations of the two single-strand species, $k_\mu$ is the backward rate constant and $C_1$ is the concentration of "dimers" with only one link.

The rate of the reaction which closes link number $i+1$ in the "zipping-up" of the double helix is assumed to be

$$v_i = k_f C_i - k_b C_{i+1} \quad . \tag{2}$$

Saunders and Ross assume that all the steps after the first have the same $k_f$ and $k_b$, and that $k_u$ and $k_b$ are equal. The first may be a reasonable approximation, especially for $i$ reasonably large, and seems an unavoidable approximation. However, it would seem unlikely the $k_b$ would equal $k_u$, since one reaction simply unzips the chains by one hydrogen-bond of many, while the other reaction completely separates the chains.

We assume $k_u \neq k_b$ and proceed in the manner of Saunders and Ross.

Multiplication of equation 2 by $(k_b/k_f)^i$ gives:

$$V_i\left(\frac{k_b}{k_f}\right)^i = k_b\left(\frac{k_b}{k_f}\right)^{i-1} C_i - k_b\left(\frac{k_b}{k_f}\right)^i C_{i+1} \quad . \tag{3}$$

We sum equation 3 over $i$ from $1$ to $N-1$ (the number of links in the chain at completion) and add equation 1, obtaining:

$$\sum_{i=0}^{N-1} V_i\left(\frac{k_b}{k_f}\right)^i = k_0 AB - k_u C_1 + k_b C_1 - k_b\left(\frac{k_b}{k_f}\right)^{N-1} C_N \,. \tag{4}$$

We now consider the rate of "zipping-up", $V$, without consideration of how far along the chain the reaction is occurring.

$$v\sum_{i=0}^{N-1}\left(\frac{k_b}{k_f}\right)^i = k_0AB - k_uC_1 + k_bC_1 - k_b\left(\frac{k_b}{k_f}\right)^{N-1}C_N \, . \qquad (5)$$

The sum is seen to be a geometric progression,

$$\sum_{i=0}^{N-1}\left(\frac{k_b}{k_f}\right)^i = \frac{1-\left(k_b/k_f\right)^N}{1-k_b/k_f} \, , \qquad (6)$$

giving

$$v = \frac{k_0AB\left(1-k_b/k_f\right)}{1-\left(k_b/k_f\right)^N} + \frac{\left(k_b-k_u\right)C_1\left(1-k_b/k_f\right)}{1-\left(k_b/k_f\right)^N} - \frac{k_b\left(k_b/k_f\right)^{N-1}C_N\left(1-k_b/k_f\right)}{1-\left(k_b/k_f\right)^N} \, . \qquad (7)$$

Now we assume that the temperature is less than the helix melting temperature, so that

$$k_b/k_f < 1 \, . \qquad (8)$$

If this is so,

$$\left(k_b/k_f\right)^N << 1 \, , \qquad (9)$$

since $N >> 1$ is assumed.

Equation 7 becomes

$$v \cong k_0AB\left(1-\frac{k_b}{k_f}\right) + \left(k_b-k_u\right)C_1\left(1-k_b/k_f\right) \, . \qquad (10)$$

The result of Saunders and Ross is lacking the last term. We assume the temperature dependence for the $k$'s :

$$k_\alpha = f_\alpha \exp\left\{-H_\alpha^{+}/RT\right\}, \alpha = o, b, f, u. \tag{11}$$

and obtain

$$\begin{aligned} V = {} & AB f_o \exp\left(-H_o^{+}/RT\right)\left[1 - \frac{f_b}{f_f}\exp\left(\Delta H/RT\right)\right) \\ & + C_1\left[f_b e^{-H_b^{+}/RT} - f_u e^{-H_u^{+}/RT}\right]\left[1 - \frac{f_b}{f_f} e^{\Delta H/RT}\right], \end{aligned} \tag{12}$$

where $\Delta H = H_f^{+} - H_b^{+}$ is the enthalpy change for one step. The analogous result of Saunders and Ross, which consists of the first line only, is used to fit some experimental data, using $H_o^{+} \approx 0$ and $\Delta H \approx$ 2 kcal mole$^{-1}$. In order to see if the data can be fit using all of equation 12, we transform equation 12 to use the independent variable $g = \exp(\Delta H/RT)$, since this was the independent variable on the graph of data, against which $V$ was a straight line of negative slope.

Equation 12 becomes

$$\begin{aligned} V = {} & AB\, f_o\, g^{-H_o^{+}/\Delta H}\left(1 - \frac{f_b}{f_f} g\right) \\ & + C_1\left[f_b g^{-H_b^{+}/\Delta H} - f_u g^{-H_u^{+}/\Delta H}\right]\left(1 - \frac{f_b}{f_f} g\right). \end{aligned} \tag{13}$$

We differentiate this to obtain the slope, obtaining:

$$\begin{aligned}\frac{dv}{dg} = AB\Big(&-\frac{f_o f_b}{f_f} g^{-H_o^+/\Delta H} - \frac{f_o H_o^+}{\Delta H} g^{-\frac{H_o^+}{\Delta H}-1} \\ &+ \frac{f_o f_b}{f_f}\frac{H_o^+}{\Delta H} g^{\frac{-H_o^+}{\Delta H}-1}\Big) + C_1\Big(-\frac{f_b^2}{f_f} g^{-H_b^+/\Delta H} \\ &+ \frac{f_u f_b}{f_f} g^{-H_u^+/\Delta H} - \frac{f_b H_b^+}{\Delta H} g^{-\frac{H_b^+}{\Delta H}-1} + \frac{f_u H_u^+}{\Delta H} g^{-\frac{H_o^+}{\Delta H}-1} \\ &+ \frac{f_b^2}{f_f}\frac{H_b^+}{\Delta H} g^{-H_b^+/\Delta H} - \frac{f_u f_b}{f_f}\frac{H_u^+}{\Delta H} g^{-H_u^+/\Delta H}\Big). \qquad (14)\end{aligned}$$

Now if Saunders and Ross assume $H_o^+ = 0$, they get a constant slope and can fit their data, since their result corresponds to the first line only of equation 14.

However, we can also get a constant slope, enabling us to fit a straight line, if we set in equation 14:

$$H_o^+ = H_u^+ = H_b^+ = 0 , \qquad (15)$$

enabling us to obtain a value for $\Delta H$. Perhaps other combinations of parameters can also be found to make $dv/dg$ constant.

We have shown that the model of Ross and Saunders, although fitting the data, is not the only one to do so, and that one which is <u>a priori</u> more appealing can also fit the data.

# REFERENCE

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