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Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics

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A new formulation of statistical thermodynamics is derived for classical fluids of molecules that tend to associate into dimers and possibly higher s-mers due to highly directional attraction. A breakup of the pair potential into repulsive and highly directionally attractive parts is introduced into the expansion of the logarithm of the grand partition function in fugacity graphs. The bonding by the directional attraction is used to classify the graphs and to introduce a topological reduction which results in the replacement of the fugacity by two variables: singlet density ρ and monomer density ρ_0. Results for the thermodynamic functions as functionals of ρ and ρ_0 are given in the form of graph sums. Pair correlations are analyzed in terms of a new matrix analog of the direct correlation function. It is shown that the low-density limit is treated exactly, while major difficulties arise when the Mayer expansion, which employs only ρ, is used. The intricate resummations required for the Mayer expansion are illustrated for the case where dimers are the only association products.

KEY WORDS: Highly directional forces; association; dimers; expansion in graphs; topological reduction.

1. INTRODUCTION

The mainstays of quantitative theories of simple and multipolar fluids are two methods: thermodynamic perturbation theory and integral equations for the pair correlations. Experience has shown that the approximation to be adopted must depend on the physical nature of the interaction. The Percus–Yevick (PY) equation$^{(1)}$ is successful for isotropic or moderately anisotropic repulsion, the hypernetted chain (HNC) equation$^{(2-7)}$ does well

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for Coulomb forces, and the SSC equation(8) is successful for multipolar and dipolar polarizable systems.(9) All of these integral equations, as well as thermodynamic perturbation theory, can be derived from a formulation where the Helmholtz free energy A is given as a functional of the singlet density ρ.

A challenging remaining problem of classical fluid theory is that of molecules with highly directional forces. If the directional forces are attractive, then they tend to promote association into dimers, trimers, and higher s-mers with conformations which depend on the geometry of the repulsion and the directional attraction. In the first two papers we restrict our attention to molecular models consisting of a hard core and a single attraction site. We believe that even this simplest case cannot be attacked successfully by merely introducing new approximations into standard methods. We consider it essential to introduce the geometry of the interaction at an early stage. In this respect our approach coincides with that of Andersen,(10,11) who previously examined such systems in two interesting papers. Incorporation of graph cancellation due to steric effects is cumbersome and inefficient in the expansion in the singlet density ρ, which serves as the conventional starting point for simple and multipolar fluids. In this respect the expansion in the fugacity z is simpler and much more effective. This dictates the choice of the z-expansion as our starting point, one that is shared with theories based on appeal to the idea of physical clusters, as exemplified by the work of Chandler and Pratt.(12)

Our subsequent development, however, is quite different from the physical cluster theories. It leads quite naturally to a formulation of statistical thermodynamics in terms of two density variables, ρ and a monomer density ρ_0. There is a strong structural similarity to the Mayer theory, which is based on ρ alone. This allows us to find analogs to the whole machinery of s-particle correlation and direct correlation functions rather easily.

From a physical point of view, the two-density theory is vastly superior. We illustrate this by examining the low-density limit of a dimerizing gas. The correct behavior is obtained trivially in the two-density theory, while the Mayer ρ-expansion requires a formidable graph resummation. This makes it unlikely that any simple integral equation based on the ρ formalism could approximate the graph sums that are required.

2. PAIR POTENTIAL

A model potential capable of representing a wide variety of physical circumstances is the following:

$$\phi(12) = \phi_R(12) + \sum_\alpha \sum_\beta \phi_{\alpha\beta}(|\mathbf{r}_2 + \mathbf{d}_\beta(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_\alpha(\Omega_1)|) \qquad (1)$$

where $i = 1, 2, \ldots$ is shorthand for the position $\mathbf{r}_i$ of the molecular center and the orientation Ω_i of molecule i; $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ are vectors from the molecular center to an interaction site. The $\phi_{\alpha\beta}$ between pairs of sites in distinct molecules are assumed to be attractive, i.e., $\phi_{\alpha\beta} \leqslant 0$. The potential $\phi_R(12)$ is taken to be the interaction of two hard particles of given shape, or at least strongly repulsive. The simplest example is the hard sphere potential

$$\phi_R(12) = \begin{cases} \infty & \text{for} \quad r_{12} < D \\ 0 & \text{for} \quad r_{12} > D \end{cases} \tag{2}$$

where D is the hard sphere diameter.

In the first two papers we specialize to a one-component system of molecules with a single attraction site. Even this reflects a wide range of physical situations. If the site coincides with the center of isotropic repulsion then we have a simple fluid, which exhibits the usual gas–liquid transition. We are interested here in the other extreme where the site of strong short-ranged attraction is located near the edge of the repulsive core. The simplest model consists of a hard sphere $\phi_R(12)$ given by (2) and a $\phi_A(12)$ of finite range:

$$\phi_A(x)\left\{ \begin{array}{lll} < 0 & \text{for} & x < a \\ = 0 & \text{for} & x > a \end{array} \right\}, \qquad x = |\mathbf{r}_2 + \mathbf{d}(\Omega_2) - \mathbf{r}_1 - \mathbf{d}(\Omega_1)| \tag{3}$$

where d must satisfy

$$\tfrac{1}{2}(D - a) < d < \tfrac{1}{2}D \tag{4}$$

The case of a site of short-ranged attraction located near the edge of the hard core is realized by the additional restriction

$$a \ll D \tag{5}$$

This has the following consequences. In any allowed configuration of any number N of molecules, each particle can take part in only one attractive interaction $\phi_A(ij) \neq 0$. If this is satisfied for the pair (ij), then the repulsive cores of i and j prevent any particle k from coming close enough to feel the influence of the attraction sites of i or j. Interactions of this type were first considered by Anderson.(10,11)

In theories formulated in terms of graphs, $\phi(12)$ appears in the form of the Mayer f-function, defined by

$$e(12) = \exp[-\beta\phi(12)], \qquad f(12) = e(12) - 1 \tag{6}$$

Here $\beta = 1/kT$, where k is Boltzmann's constant and T is the Kelvin temperature. In our analysis we use the standard decomposition

$$f(12) = f_R(12) + F(12), \qquad F(12) = e_R(12) f_A(12) \tag{7}$$

3. FUGACITY GRAPHS

For uniform systems the pressure p is related to the grand partition function Ξ by $\beta pV = \ln \Xi$. The latter quantity can be expressed as a sum of graphs, whose points i carry factors $z(i)$, given by

$$z(i) = \Lambda \exp \beta\left[\mu - U(i)\right]$$

where Λ is the contribution to the partition function from the integration over translational and rotational momenta, μ is the chemical potential, and $U(i)$ is an external potential. For the uniform system we are concerned with $U(i) = 0$, and $z(i)$ becomes the constant fugacity z. We have[3]

$\ln \Xi$ = sum of all connected graphs composed of z-points and f-bonds. All points are field points. The single point with no bonds is included.

$\rho(1)$ = graphs obtained from $\ln \Xi$ by taking all ways of turning one field point into a labeled point 1.

For a uniform system the singlet density $\rho(1)$ is a constant related to the number density $\bar{\rho}$ by $\rho(1) = \bar{\rho}/\Omega$, where Ω is the integral over orientations. In the absence of special molecular symmetry $\Omega = 8\pi^2$.

Our analysis begins by using (7) to generate a new set of z-graphs by taking all ways of replacing each $f(ij)$ by $f_R(ij)$ or $F(ij)$. The use made of these new graphs is rather different from the usual practice of liquid state theory. It is based on an idea due to Lockett,(14) who used it in a quite different context, nucleation in simple fluids.

Consider the set of z-graphs on s points, with f_R-bonds or F-bonds. A subset of them is the set in which all s points are connected by paths of F-bonds. This subset can be constructed in two steps: (1) construct all connected graphs on s points with all bonds F-bonds, (2) for any pair (ij) not connected by the direct bond $F(ij)$, insert a bond $e_R(ij)$. Since the s points are already connected after step (1), all pairs lacking the direct F-bonds receive the sum of no bond and a direct f_R-bond in step (2). Borrowing terminology from chemistry, we refer to the F-connected graphs filled with e_R-bonds on $2, 3 \ldots$ few $\ldots s$ points as dimer, trimer $\ldots$ oligomer $\ldots$ s-mer graphs. The single point without bonds is included as a monomer graph. The s-mer graphs with $s \leqslant 4$ are shown in Fig. 1.

We may now reexpress the set of all connected z graphs as follows:

$\ln \Xi$ = sum of all connected graphs consisting of s-mer graphs ($s = 1 \ldots \infty$) and f_R-bonds between pairs of points in distinct s-mer graphs.

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[3] For a review of graph theory see Ref. 13.

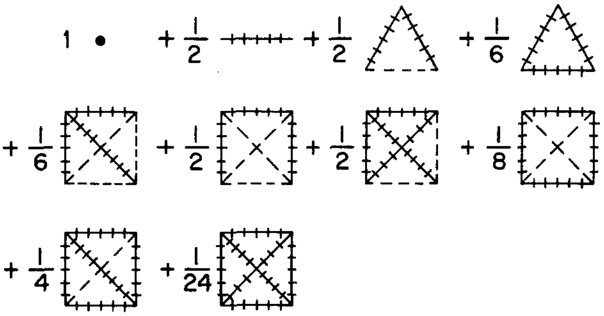

Fig. 1. The s-mer graphs contained in $\ln \Xi$ for $s = 1$ through $s = 4$. The crossed bonds are F-bonds, the dashed bonds are e_R-bonds.

The rule for obtaining $\rho(1)$ from $\ln \Xi$ is unchanged. The idea of using the s-mer graphs to classify the set of all graphs is found in the work of Lockett.(14)

4. STERIC INCOMPATIBILITY

The process of filling connected F-graphs with e_R-bonds optimizes the cancellation due to steric incompatibility (SI) of the bonds. For the short-ranged attraction expressed by (2)–(5) all s-mer graphs for $s > 2$ vanish due to SI. This occurs because they all contain either a triangle of two F-bonds and one e_R-bond as shown in Fig. 2, or a triangle of F-bonds, which has the same effect since $F(ij)$ contains $e_R(ij)$ as a factor. This type of SI was used by Andersen,(10,11) who considered it a model for hydrogen bonding. This work used the density expansion, where the effect of SI is weaker and more difficult to apply. Incidentally, the type of SI shown in Fig. 1 can occur even for a simple fluid, if an attractive region inside a hard core is allowed. Such a model was used by Høye and Olaussen,(15) and more recently by Cummings and Stell.(16)

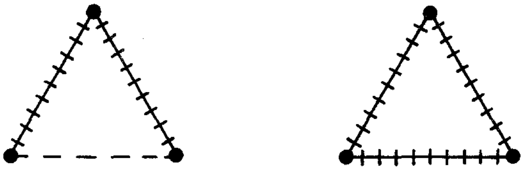

Fig. 2. Configuration of bonds which causes vanishing of a graph due to steric incompatibility for certain interactions.

We can construct potentials of the form (2)–(4) which allow trimers, but not tetramers, or have a cutoff at some higher $s = S$. As long as S is finite, or at least a reasonably small number, we would expect increasing association with decreasing T, but no gas–liquid transition. On this basis one may conjecture that the gas–liquid transition is related to the catastrophic increase with s of allowed s-mer graphs when no cutoff due to SI is provided.

Consider the case where SI allows oligomer graphs up to a small integer S. Let the density be low, but let T be so low that $F(ij)$ takes on very large values, so that appreciable association remains. A physically sensible description in terms of z is the retention of only the pure s-mer graphs $G[s, \alpha(s)]$, where $\alpha(s)$ runs over the topologically distinct s-mer graphs. Then we have

$$\beta p V = M(z) \tag{8}$$

$$N = zM'(z) \tag{9}$$

$$M(z) = \sum_{s=1}^{S} \sum_{\alpha(s)} G[s, \alpha(s)] z^s \tag{10}$$

Here $G[s, \alpha(s)] z^s$ represents the number of s-mers of type α, and $G[s, \alpha(s)] z^s s$ the number of monomeric units contained in them. The z-independent numbers $G[s, \alpha(s)]$ represent equilibrium constants in the law of mass action.

Away from the low-density limit it is necessary to include graphs containing more than one oligomer graph. Here the z-graphs are no longer the best formulation. The crucial step which leads to a useful formalism is a topological reduction which eliminates articulation points. It is analogous to going from z-graphs to ρ-graphs in the Mayer formalism.(13)

5. TOPOLOGICAL REDUCTION

We consider $\rho(1)$ as a sum of z-graphs and assign each graph to one of two classes. If the labeled point 1 is a monomer point, i.e., has no incident bond $F(1i)$, then the graph is in $\rho_0(1)$. If 1 is an s-mer point with $s \geqslant 2$, then the graph is in $\rho_1(1)$:

$$\rho(1) = \rho_0(1) + \rho_1(1) \tag{11}$$

The graphs in $\rho_0(1)$ and $\rho_1(1)$ with up to three points are shown in Fig. 3.

Physically, ρ_0 is a monomer density; it was introduced in a different context by Lockett.(14)

We analyze the graph sums $\rho_0(1)$ and $\rho_1(1)$ in terms of the connectivity at the labeled point 1. Here and subsequently all graphs are taken as

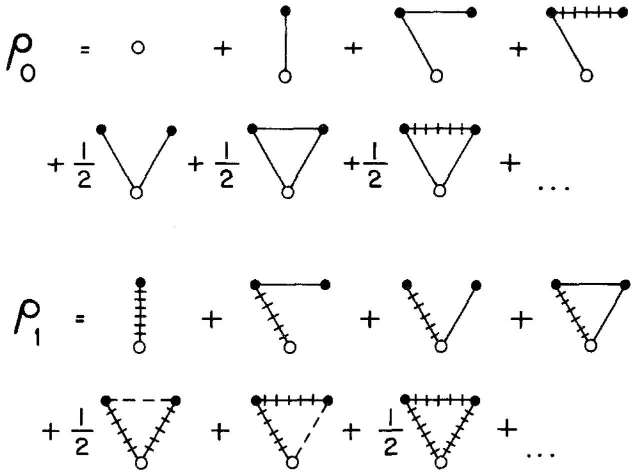

Fig. 3. The graphs in $\rho_0(1)$ and $\rho_1(1)$ up to three points. The open circle is the labeled point 1. All points carry factors z. The plain solid lines are f_R-bonds.

composed of s-mer subgraphs, $s = 1 \ldots \infty$, and f_R-bonds. Each *s-mer subgraph is counted as irreducible*, i.e., both its F-bonds and its e_R-bonds count as bonds. In other words, the e_R-bonds in an s-mer are *never* broken up into $1 + f_R$.

By a standard combinatorial argument, the sum of all graphs in $\rho_0(1)/z$ is equal to the exponential of a graph sum $c_0(1)$ which is the subset of graphs in $\rho_0(1)/z$ that remain connected when all connections at 1 are broken. Thus

$$c_0(1) = \ln[\rho_0(1)/z] \tag{12}$$

The graph sum $\rho_1(1)$ contains $\rho_0(1)$ as a factor. The quotient $\rho_1(1)/\rho_0(1)$ consists of all graphs which remain connected when all connections at 1 are broken, with 1 being part of an s-mer, $s \geqslant 2$. This graph sum defines $c_1(1)$:

$$c_1(1) = \rho_1(1)/\rho_0(1) \tag{13}$$

The graph sums $c_0(1)$ and $c_1(1)$ contain both reducible and irreducible graphs when written as z graphs. Each of the $c_i(1)$ can be reexpressed as its subset of graphs free of articulation points, by associating with every field point instead of z a factor which expresses all that the graphs that can be tacked on, namely,

$$\left.\begin{matrix} \rho(i) \\ \rho_0(i) \end{matrix}\right\} \quad \text{if } i \text{ is } \left\{\begin{matrix} \text{a monomer} \\ \text{an } s\text{-mer, } s \geqslant 2 \end{matrix}\right\} \text{ point} \tag{14}$$

$c_0(1)$ and $c_1(1)$ have now been expressed as sums of irreducible, i.e., doubly connected, graphs. It is clear that they belong to a hierarchy of functions based on $c^{(0)}$, characterized below.

> $c^{(0)}$ = sum of all irreducible graphs consisting of monomer points carrying factors of ρ, s-mer subgraphs with $s \geqslant 2$ and every point carrying a factor ρ_0, and f_R-bonds between some pairs of points in distinct s-mers.

All points are field points, so that $c^{(0)}$ is extensive, i.e., proportional to V. The graphs in $c^{(0)}$ on two, three, and four points are shown in Fig. 4.

It is evident that the quantities $c_0(1)$ and $c_1(1)$ are just the two functional derivatives

$$c_0(1) = \partial c^{(0)} / \partial \rho(1) \tag{15}$$

$$c_1(1) = \partial c^{(0)} / \partial \rho_0(1) \tag{16}$$

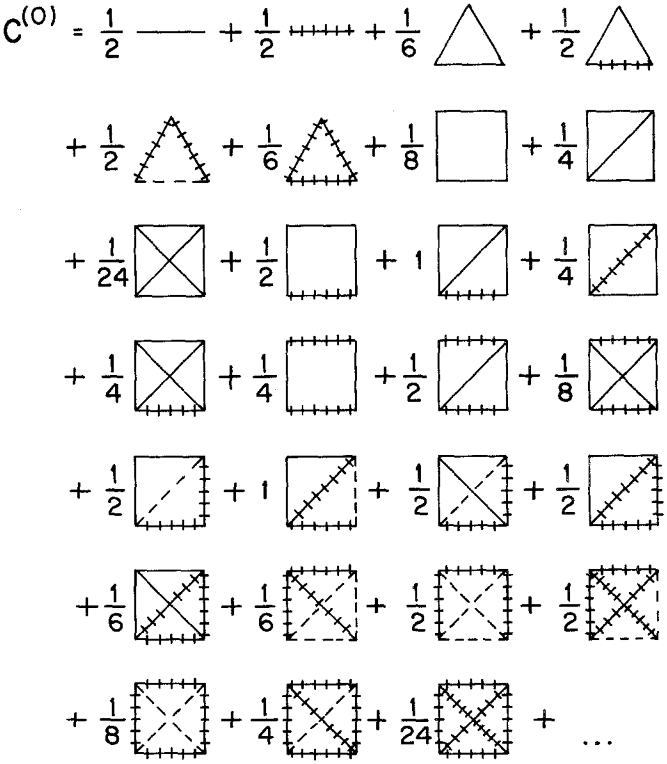

Fig. 4. The graphs in $c^{(0)}$ up to four points. Monomer points carry factors ρ, s-mer points with $s \geqslant 2$ carry factors ρ_0.

which correspond to taking all ways of turning a field point into a point labeled 1 and deleting the factor ρ or ρ_0 associated with it.

6. THERMODYNAMICS

We can now derive graphical expressions for p and A in terms of $c^{(0)}$ and quantities derived from it. Let us anticipate the result for the pressure of a uniform system,

$$\beta p V = \int \rho_0(1)\, d(1) - \int \rho(1) c_0(1)\, d(1) + c^{(0)} \tag{17}$$

and verify that it is correct.[4] We take a variation of (17). On the right-hand side we use

$$\delta c^{(0)} = \int c_1(1) \delta\rho_0(1)\, d(1) + \int c_0(1) \delta\rho(1)\, d(1) \tag{18}$$

$c_1(1)$ is eliminated by the use of (13). For $\delta c_0(1)$ we substitute the differential of (12), namely,

$$\delta c_0(1) = \frac{\delta\rho_0(1)}{\rho_0(1)} - \frac{\delta z}{z} \tag{19}$$

With these substitutions, the variation of (17) is

$$\delta(\beta p) V = \frac{\delta z}{z} \int \rho(1)\, d(1) \tag{20}$$

which is the required result $(\partial p / \partial \mu)_\beta = \bar{\rho}$.

From the result for p, we can immediately obtain an expression for $A = N\mu - pV$. We find that

$$\beta A = \int \left[\rho(1) \ln \frac{\rho_0(1)}{\Lambda} - \rho_0(1) \right] d(1) - c^{(0)} \tag{21}$$

It is noteworthy that the subsidiary conditions (12) and (13), derived by topological graph reduction, are completely equivalent to the result of minimizing A, as given by (21), with respect to $\rho(1)$ and $\rho_0(1)$ while imposing a fixed number N of particles. In

$$\delta\left[\beta A - \lambda \int \rho(1)\, d(1) \right] = 0 \tag{22}$$

the variation with respect to ρ_0 recovers (13), while the variation with respect to ρ recovers (12) with the Lagrange multiplier λ identified as

$$\lambda = \ln(z/\Lambda) = \beta\mu \tag{23}$$

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[4] While ρ and ρ_0 are constants for a uniform system, it is convenient to carry along the explicit argument.

This reflects the chemical equilibrium condition that a monomeric unit must be at equal chemical potential whether it is a free monomer or bound in an s-mer, $s \geqslant 2$.

Consider again the case where ρ is low enough to imply small effect of repulsive interaction between oligomers, but high enough so that appreciable association due to low T remains. The reasonable approximation in obtaining the thermodynamics from (17) or (21) is once again the retention of only the pure s-mer graphs in $c^{(0)}$. Then we obtain

$$c^{(0)} = M(\rho_0) - \rho_0 \tag{24}$$

Since $c^{(0)}$ in this limit does not contain ρ, Eq. (12) implies

$$\rho_0 = z \tag{25}$$

and by use of (13) we recover exactly Eqs. (8)–(10). The exact treatment of the low-density case by the z-formalism is reproduced exactly by the two-density formalism. By contrast, the Mayer expansion in ρ alone is eminently unsuccessful, as elucidated in Section 8. The difficulty is of course due to the large values attained by the F-bonds for low T. In the method based on ρ *and* ρ_0, the increasingly large F's as T is lowered promote increasing association and consequent depletion of monomers. The resulting decrease in the values of ρ_0, which is associated with the s-mer points for $s \geqslant 2$, serves to suppress the catastrophe due to large F which occurs in the Mayer formalism. Indications of the suppression of the effect of large F were also obtained by Andersen(10) using a different and less clear-cut calculation.

More explicitly, for the system where the dimer is the only nonvanishing s-mer with $s > 1$ we have at low density

$$\rho = \rho_0 + \rho_0^2 I, \qquad I = \int e_R(12) f_A(12)\, d(2) \tag{26}$$

$$\lim_{I \to \infty} (\rho_0^2 I) = \rho \tag{27}$$

At higher density, $e_R(12)$ is replaced by $g_{00}(12)$, defined in Section 7. In view of the qualitative similarity between these two quantities, Equations (26) and (27) suggest that at low T and moderate ρ the graphs with s points and n F-bonds are comparable to graphs with $s - n$ points and no F-bonds. This is consistent with retaining ρ_0 and the dimer graph in lowest order.

7. CORRELATION FUNCTIONS

By using the theory of graphs, the entire formalism of s-particle ordinary and direct correlation functions can be transplanted to the two-density formalism. The analogs of the s-particle direct correlation functions are given by

$$c_{00\ldots 11\ldots}(ij\ldots mn\ldots) = \frac{\partial^s c^{(0)}}{\partial\rho(i)\partial\rho(j)\ldots\partial\rho_0(m)\partial\rho_0(n)\ldots} \tag{28}$$

The subscript corresponding to a labeled point k is

$$\left.\begin{matrix}0\\1\end{matrix}\right\} \quad \text{if } k \text{ is} \left\{\begin{matrix}\text{a monomer}\\ \text{an } s\text{-mer, } s \geqslant 2\end{matrix}\right\} \text{ point} \tag{29}$$

The process of rewriting z-graphs in terms of s-mer graphs and f_R-bonds affects bonds, but not points. Therefore, the usual way of obtaining the truncated s-particle distribution functions $\hat{\rho}(1\ldots s)$ from $\ln\Xi$ are unchanged. We require all ways of turning s points into points labeled $1\ldots s$, corresponding to the functional differentiation

$$\hat{\rho}(1\ldots s) = z(1)\ldots z(s)\frac{\partial^s(\ln\Xi)}{\partial z(1)\ldots\partial z(s)} \tag{30}$$

Similarly unchanged is the expression for the complete s-particle distribution function $\rho(1\ldots s)$. It is the sum over all partitions into subsets of $1\ldots s$ of the product of the $\hat{\rho}_t$ of the subsets, e.g.,

$$\rho(1) = \hat{\rho}(1), \qquad \rho(12) = \hat{\rho}(12) + \hat{\rho}(1)\hat{\rho}(2) \tag{31}$$

The same topological reduction as before converts each graph sum $\hat{\rho}(1\ldots s)$ into its subset free of articulation points, but with bridge points permitted, with each point k, labeled or field point, carrying a factor of $\rho(k)$ or $\rho_0(k)$ according to the rule in Eq. (14).

The resulting expression for $\hat{\rho}(1\ldots s)$ in terms of connected graphs with ρ points and ρ_0 points is a logical basis for splitting it into 2^s terms according to the factors at the labeled points. In the most important case, $s = 2$, we have

$$\begin{aligned}\hat{\rho}(12) = {} & \rho(1)h_{00}(12)\rho(2) + \rho(1)h_{01}(12)\rho_0(2)\\ & + \rho_0(1)h_{10}(12)\rho(2) + \rho_0(1)h_{11}(12)\rho_0(2)\end{aligned} \tag{32}$$

Similar equations hold for higher s. Functions $g_{ij}(12)$ are defined by an equation of the same form as (32), with $\rho(12)$ replacing $\hat{\rho}(12)$ and g replacing h. Thus, we have

$$h_{ij}(12) = g_{ij}(12) - \delta_{i0}\delta_{j0} \tag{33}$$

which is sensible, since the entire constant asymptotic form of $\rho(12)$ is contained in the term in $g_{00}(12)$.

For any s, the graphs in $\hat{\rho}(1\ldots s)$ may be analyzed in terms of bridge points to obtain an analog of the s-particle Ornstein–Zernike equation. The basic condition which applies at the bridge point is this: at most one of the subgraphs sharing it may have an F-bond incident on the bridge point. For

$s = 2$ this leads to the matrix equation

$$h_{ij}(12) = c_{ij}(12) + \sum_{k=0}^{1} \sum_{l=0}^{1} \int c_{ik}(13)\rho_{kl}(3)h_{lj}(32)\,d(3) \tag{34}$$

where the matrix ρ_{ij} has elements

$$\rho_{00} = \rho, \qquad \rho_{01} = \rho_{10} = \rho_0, \qquad \rho_{11} = 0 \tag{35}$$

This raises the question of the compressibility theorem for uniform fluids, which can be formulated either in terms of $g(12)$, or the direct correlation function $c(12)$. The first form may be written

$$\beta^{-1}\bar{\rho}(\partial\bar{\rho}/\partial p) = \bar{\rho} + \int \hat{\rho}(12)\,d(2)\,d\Omega_1 \tag{36}$$

This form may be expressed in terms of the $h_{ij}(12)$ using (32). On the other hand, there is no simple relation between the ordinary direct correlation function $c(12)$ and our $c_{ij}(12)$. The required relation in terms of the $c_{ij}(12)$ is derived in paper II in connection with integral equation theories.

8. RELATION TO MAYER EXPANSION

The goal of the two-density formalism is the creation of a suitable framework for introducing well-defined approximation schemes for associating fluids. Any such scheme which treats the allowed pure s-mer graphs exactly is guaranteed to reproduce exact results for the otherwise troublesome limit of low density with strong association and consequent depletion of monomers.

It appears worthwhile to demonstrate by explicit calculation that it is very difficult to recover the correct behavior if the starting point is the Mayer theory, which uses only ρ. Then the fundamental expressions are(13)

$$\beta pV = \int \rho(1)\,d(1) - \int \rho(1)c(1)\,d(1) + c^{(0)} \tag{37}$$

$$\beta A = \int \rho(1)\left[\ln\frac{\rho(1)}{\Lambda} - 1\right]d(1) - c^{(0)} \tag{38}$$

Here $c^{(0)}$ is *not* the quantity used in the two-density formalism. It is defined in the usual way,

$c^{(0)}$ = sum of all irreducible graphs of f_R-bonds and/or F-bonds. All points k carry a factor $\rho(k)$. Also, $c(1) = \partial c^{(0)}/\partial\rho(1)$.

The fact that the graphical expression for $c^{(0)}$ becomes divergent for low T is a mathematical and relatively minor defect. Analytic continuation by resummation is available, though not obvious. The really important defect is this. Due to the restriction to irreducible graphs, sets of points connected by paths of F-bonds do not always occur "filled with e_R-bonds." As a result the incidence of SI of bonds is very low compared to the set of connected graphs in the z-expansion. In the case where physically, and in the two-density formalism, only dimers are permitted, all configurations of F-bonds must be considered. In the following we perform the required resummation for the dimerizing gas in the low-density limit.

Consider a set of points and a given set of F-bonds, and demand the construction of all ways of making an irreducible graph by adding f_R-bonds. If the skeleton of F-bonds contains a ring of $n \geqslant 4$ points then any added bonds inside the ring are irrelevant to the reducibility or irreducibility of the graph. Hence, in counting all irreducible graphs the interior of the ring is filled with e_R-bonds. This produces n-fold SI, and these graphs sum to zero. A ring of three F-bonds also vanishes due to SI, because $F(ij)$ contains $e_R(ij)$ as a factor.

We are left with graphs such that the F-skeleton consists of one or more trees. In the limit of low ρ and T, where F but not f_R becomes large, we are required to retain all graphs containing a single tree of F-bonds, and no monomer points. Even this restricted resummation is not easy.

Consider a specific tree composed of points connected by F-bonds. Take any irreducible graph obtained by adding f_R-bonds between some pairs of points (i, j) of the tree. We define a maximal f_R-bond as follows. Connection of points (i, j) by $f_R(ij)$ defines a set $S(i, j)$ consisting of i, j and all points on the unique path of F-bonds from i to j. Given the presence of $f_R(ij)$, an f_R bond between any other pair of points in $S(i, j)$ is *not* maximal. By deleting all f_R bonds which are not maximal in some set S generated by another f_R-bond, we can reduce any irreducible graph to a unique irreducible graph in which *all* f_R-bonds are maximal.

We can go in the opposite direction and generate all irreducible graphs starting from the subset with only maximal f_R-bonds. This is done as follows. For any pair of points (k, l) which belong to $S(i, j)$ for some maximal $f_R(i, j)$ and are not connected by $F(kl)$, we insert an $e_R(kl)$, implying either presence or absence of $f_R(kl)$. O course, the pair (k, l) may lie on more than one path of F-bonds connecting the ends of a maximal f_R bonds. By this construction each irreducible graph arises from only one irreducible graph with only maximal f_R-bonds.

Clearly, this construction fills the interior of any loop consisting of a maximal $f_R(ij)$ and a path of $d \geqslant 3$ F-bonds from i to j with e_R-bonds. A single such filled loop in a graph is sufficient to induce vanishing due to SI. Hence, the only surviving graphs are those for which the maximal $f_R(ij)$ are also minimal, i.e., i and j are connected by an F-path of length $d = 2$.

The graphs with $d = 2$ are discussed most easily by associating with each f_R-bond the unique point of the tree which is skipped over. In evaluating the integral represented by the graph, each f_R-bond can be replaced by -1, by virtue of the SI condition of Fig. 1. We still need to solve the combinatorial problem of counting the number of ways maximal f_R-bonds with $d = 2$ can be added to make an irreducible graph. Let m be the number of F-bonds incident on a point of the tree. No f_R-bonds are associated with a point with $m = 1$. Only one possible f_R-bond can be associated with a point i with $m = 2$. This bond must certainly be added, for otherwise the two parts of the tree connected at i could not be rendered doubly connected. For $m > 2$ we require any connected graph of f_R-bonds on the m adjacent points. Let these points be labeled $1 \ldots m$. Suppose that point 1 is bounded by $f_R(1i)$ to k other points, $2 \leqslant k \leqslant m$. Then additional connections between pairs of the k points are irrelevant to the connectivity, and we get all connected graphs by filling with e_R-bonds. This induces vanishing by SI. Hence, the only surviving graphs are those with $k = 1$. We obtain a factor -1 for the f_R-bond, and a factor $(m - 1)$ for the number of possible connections. We remove the point 1 from the set and repeat the argument with the remaining $m - 1$ points. The process stops when the set of points is exhausted. The total factor picked up is $(-1)^{m-1}(m-1)!$

The result is the following. The appropriate limit of $c^{(0)}$ of Mayer theory is obtained by evaluating all the integrals represented graphically by trees of F-bonds, including the proper combinatorial weight, and then summing them with an additional factor

$$\sum_{\substack{\text{inner} \\ \text{points } i}} (-1)^{m(i)-1}\left[m(i) - 1\right]! \tag{39}$$

An inner point is one with $m \geqslant 2$.

There is a standard way of simplifying the combinatorial problem of carrying out this sum. We turn one point into a labeled point, i.e., we consider $c(1)$ rather than $c^{(0)}$. At the point 1 we can have attached number $m \geqslant 1$ of trees. The sum of all trees that can be attached is a quantity Q. The symmetry number by which we must divide to obtain the correct weight is $m!$, and the factor associated with the multiplicity (39) is $(-1)^{m-1}(m-1)!$ Hence we obtain

$$c(1) = \sum_{m=1}^{\infty} (-1)^m Q^m / m = \ln(1 + Q) \tag{40}$$

Q consists of trees of F-bonds with exactly one bond from 1 to an adjacent point, which we may call 2. If this bond is the whole tree, then we have exactly ρI, where I is the integral defined in (26). We may also have attached at 2 any number $m \geqslant 1$ of trees in Q. The correct combinatorial weight is $1/m!$ The coefficient due to the multiplicity is $(-1)^m m!$, because the number of incident F bonds is $m + 1$. Hence, the total coefficient for all possible attachments, including none, is

$$1 + \sum_{m=1}^{\infty} (-1)^m Q^m = (1 + Q)^{-1} \tag{41}$$

By transposing this factor to the left-hand side, we obtain the result

$$Q(Q + 1) = \rho I \tag{42}$$

Equations (40) and (42) express $c(1)$ as a function of ρ. The equivalence to the low-density results obtained in Sections 4 and 6 is made evident by identifying

$$Q = zI = \rho_0 I \tag{43}$$

The graph resummations can be extended to pair functions. For example, the direct correlation function $c(12)$ can be obtained in the same limit. One verifies that it is the iterative solution of the Ornstein–Zernike equation

$$h(12) = c(12) + \int c(13)\rho(3)h(32)\,d(3) \tag{44}$$

with $h(12)$ taking the low-density limit

$$h(12) = \left[\rho_0(1)\rho_0(2)/\rho(1)\rho(2)\right]F(12) \tag{45}$$

We believe that it is not profitable to follow the resummation route any further. It appears unlikely that simple integral equation closures combined with (44) can yield satisfactory approximations to the intricate resummations that had to be carried out. It seems much more sensible to base approximations directly on the two-density formalism, which guarantees the correct low-density limit even for the strongly associated state. This program is carried out in paper II.

9. CONCLUSION

We have developed a comprehensive formalism for the statistical thermodynamics of associating systems with a single molecular attraction site. It is based on the use of two density parameters and exhibits many analogies to the usual single-density formalism. The need for two densities arises quite naturally from a graph classification scheme which is found to be highly relevant outside its original realm of application.(14) It optimizes the exploitation of steric incompatibility effects, which were previously noted and used in a different formalism by Andersen.(10,11) The unsuitability of the single-density formalism has been documented by tracing the difficult resummations required to obtain results that follow trivially in the two-density formalism we have developed.

A few words are in order concerning application to chemical systems. Our use of classical statistical mechanics for rotation of the monomeric units is valid only if the monomers are molecular rather than atomic. The replacement of the discrete set of quantum mechanical vibrational states of a dimer by a classical continuum of bound states is an approximation which is best when the level spacing is small compared to kT.

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REFERENCES

1. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
2. T. Morita and K. Hiroike, *Prog. Theor. Phys.* **23**:1003 (1960).
3. J. M. van Leeuwen, J. Groeneveld, and J. deBoer, *Physica* **25**:792 (1959).
4. M. S. Green, *J. Chem. Phys.* **33**:1403 (1960).
5. E. Meeron, *J. Math. Phys.* **1**:192 (1960).
6. G. S. Rushbrooke, *Physica* **26**:259 (1960).
7. L. Verlet, *Nuovo Cimento* **18**:77 (1960).
8. M. S. Wertheim, *Molec. Phys.* **26**:1425 (1973).
9. E. L. Pollock, B. J. Alder, and G. N. Patey, *Physica* **108A**:14 (1981).
10. H. C. Andersen, *J. Chem. Phys.* **59**:4717 (1973).
11. H. C. Andersen, *J. Chem. Phys.* **61**:4985 (1974).
12. D. Chandler and L. R. Pratt, *J. Chem. Phys.* **65**:2925 (1976).
13. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964), pp. II-171-261.
14. A. M. Lockett III, *J. Chem. Phys.* **72**:4822 (1980).
15. J. S. Høye and K. Olaussen, *Physica* **104A**:435 (1980).
16. P. T. Cummings and G. Stell, *Molec. Phys.* **51**:253 (1984).