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Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites

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We derive a reformulation of statistical thermodynamics for fluids of molecules which interact by highly directional attraction. The molecular model consists of a repulsive core and several sites of very short-ranged attraction. We explore the relationship between graph cancelation in the fugacity expansion and three types of steric incompatibility between repulsive and attractive interactions involving several molecules. The steric effects are used to best advantage in a limited regrouping of bonds. This controls the density parameters which appear when articulation points are eliminated in the graphical representation. Each density parameter is a singlet density for a species consisting of molecules with a specified set of sites bonded. The densities satisfy subsidiary conditions of internal consistency. These conditions are equivalent to a minimization of the Helmholtz free energy A. Graphical expressions for A and for the pressure p are derived. Analogs of the s-particle direct correlation functions and of the Ornstein–Zernike equation are found.

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

1. INTRODUCTION

In two recent papers,(1,2) referred to in the text as I and II, we dealt with the statistical mechanics of fluids with highly directional attractive forces. The molecular model consisted of a repulsive core and short-ranged attraction mediated by a single attraction site. In I we gave a reformulation of statistical thermodynamics in terms of *two* densities, the usual singlet density ρ, and the monomer density ρ_0. An attractive feature of this theory of associating systems is the strong structural similarity to the usual statistical thermodynamics of simple and multipolar fluids, where only ρ is used. This

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similarity was exploited in deriving approximation methods that have time-tested analogs in the formulation based on ρ alone. These two-density versions of thermodynamic perturbation theory and integral equation methods were given in II.

Since short-ranged, highly directional attraction is an obvious model for chemical binding, the case of monomeric units containing multiple attraction sites is of even greater interest. In the following we present a reformulation of statistical thermodynamics for the case of several such sites. As in the case of a single site, the most significant previous work is that of Andersen,(3,4) who used somewhat different methods.

It seems appropriate to summarize the physical ideas behind the formalism. Although the model is one of site–site interactions, we avoid the frequently used reduction to a level of description where sites replace molecules as primary units.(5–10) The opposite extreme consists of treating all association products as molecules with internal degrees of freedom. While this may be desirable in principle, it almost immediately becomes prohibitively complicated. Our approach is best described as one in which there are several species of particles. *Each species represents a monomeric unit in which a specified set of attraction sites is bonded.*

The decision whether a site is bonded is not made by an appeal to the physical cluster idea,(11,12) which represents a separate line of development. Instead it relies on the clearly defined process of using graph theory after writing the total pair potential as a sum of core–core and site–site potentials and introducing Mayer f-functions for the individual terms. In this form graphs become a very flexible instrument, because they incorporate the relevant information concerning the geometry of the interactions in a form which is accessible and susceptible to physically motivated manipulations. In practice this means that we can do a regrouping which controls the density parameters that are produced when articulation points are eliminated by topological reduction.(13) Thus a great deal of physics can be incorporated in going from fugacity graphs to density graphs. That these advantages are totally lost in the reduction to a single density based on the total f-bond has been documented in the analysis of dimer-forming systems in I.

This paper contains the mechanics and physical justification of the reformulation. Possible approximation theories are discussed in a companion paper.(14)

2. PAIR POTENTIALS

We consider molecular models consisting of a repulsive core and some number M of attraction sites. We denote the set of all attraction sites by Γ, subsets of Γ by small greek letters, and individual sites by capital letters. The pair potential of two identical molecules is then

$$\Phi(12) = \Phi_R(12) + \sum_{A \in \Gamma} \sum_{B \in \Gamma} \Phi_{AB}(x_{AB}) \tag{1}$$

$$\mathbf{x}_{AB} = \mathbf{r}_2 + \mathbf{d}_B(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_A(\Omega_1) \tag{2}$$

Here $\mathbf{r}_k$ and Ω_k denote the position of the center and the orientation of molecule k; $\mathbf{d}_A$ is the vector from the molecular center to site A. Numbers $k = 1, 2, \ldots$ are shorthand for $\mathbf{r}_k$ and Ω_k. $\Phi_R(12)$ is assumed to be strongly repulsive, possibly the interaction of two—not necessarily spherical—hard cores. The site–site interactions are assumed to be purely attractive or zero, i.e., we reserve the possibility that site A interacts only with *some* sites in another molecule:

$$\Phi_{AB}(12) \geqslant 0 \tag{3}$$

For any potential $\Phi(12)$, which may be $\Phi_R(12)$ or one of the $\Phi_{AB}(12)$, we define the e-function and the f-function in the usual way by

$$e(12) = \exp[-\beta\Phi(12)], \qquad f(12) = e(12) - 1 \tag{4}$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the Kelvin temperature.

By the product property of the e-function we have

$$e(12) = e_R(12) \prod_{A \in \Gamma} \prod_{B \in \Gamma} e_{AB}(12) \tag{5}$$

$$f(12) = f_R(12) + e_R(12) \left\{ \prod_{A \in \Gamma} \prod_{B \in \Gamma} [1 + f_{AB}(12)] - 1 \right\} \tag{6}$$

A convenient graphical representation exhibits the molecule as a large open circle, the sites as small solid circles inside, labeled by type of site. The functions $f_R(12)$ and $e_R(12)$ are shown as solid and dashed lines, respectively, connecting the peripheries of the large circles 1 and 2. The site–site bond $f_{AB}(12)$ is indicated by a solid line connecting site A in 1 to site B in 2. The large circles are referred to as *hyperpoints*. A site A in i is called *bonded* if it has one or more $f_{AB}(ij)$ bonds incident. These graphs keep an account of the bonding of sites, and are not intended to represent the actual molecular geometry.

For the case of two identical molecules with sites of type A and B, with the proviso of no interaction between like sites, $f_{AA}(12) = f_{BB}(12) = 0$, we obtain from $f(12)$ the four terms shown in Fig. 1.

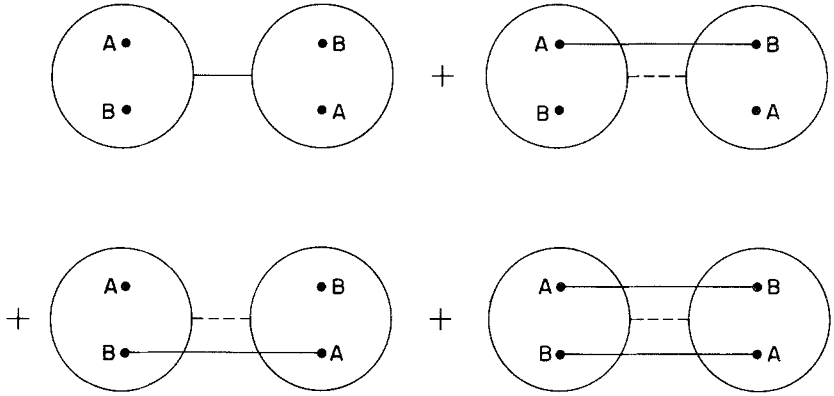

Fig. 1. The four bonding states for a pair of identical molecules with two inequivalent attraction sites, with no bonding between like sites. There are 16 bonding states if all possible site–site bonds can occur.

3. CONNECTIVITY OF FUGACITY GRAPHS

As in I, the starting point is the graphical expression for the logarithm of the grand partition function Ξ, which for a uniform system is related to the pressure p by

$$\beta p V = \ln \Xi \tag{7}$$

where V is the volume of the system. The expressions for $\beta p V$ and the singlet density $\rho(1)$ are$^{(13)}$ as follows:

$\beta p V$ = 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 $\beta p V$ by taking all ways of turning one field point into a point labeled 1.

Here $z = \Lambda \exp(\beta\mu)$, where Λ is the contribution to the partition function of the integration over translational and rotational momenta of a molecule, and μ is the chemical potential.

The decomposition of the total f-function by (6) results in the replacement of points by hyperpoints containing sites. Each total $f(12)$ is replaced either by $f_R(12)$ or one or more bonds of type $f_{AB}(12)$ in parallel with $e_R(12)$. The hyperpoints 1 and 2 count as directly connected if there is either an $f_R(12)$ or any $f_{AB}(12)$. Therefore we have, rather trivially, the following:

$\beta pV =$ sum of all connected graphs composed of z-hyperpoints and bonds. A bonded pair i, j has either $f_R(ij)$, or $e_R(ij)$ and one or more bonds of type $f_{AB}(ij)$. The single point without bonds is included.

$\rho(1) =$ all graphs obtained from βpV by taking all ways of turning a field hyperpoint into a hyperpoint labeled 1.

The issue to be faced next is the following: to what extent is it profitable to combine bonding by $f_R(ij)$ and lack of bonding between i and j into a combined bond $e_R(ij)$? In I, where we dealt with a single molecular attraction site, the combined bond $e_R(ij)$ was adopted for all pairs of points connected by a network of attraction bonds. This criterion, applied to hyperpoints with multiple sites, would not produce optimal results, because the information concerning bonding of individual sites would be discarded in making the decision. In order to achieve useful incorporation of this information, it is necessary to refine the analysis by pursuing the connectivity by attraction bonds down to the *site* level. We present the formalism that achieves this goal. The physical justification is postponed to Section 4.

As in I, we begin by considering the subclass of connected graphs such that all hyperpoints are connected by networks of attraction bonds. Denote this class by $\{S\}$. Since the hyperpoints are already connected, a bond $f_R(ij)$ may be present or absent between any pair i, j. Consider the situation in the absence of any f_R-bonds. We can break down the connectedness property between *hyperpoints* into two kinds of connectedness between *sites*.

We define: two sites A and B are *bond-connected* if and only if there is a path consisting of *attraction bonds* and *attraction sites* from A to B.

We define: two sites are *constraint-connected* if and only if they are located in the same hyperpoint.

A graph in $\{S\}$ may contain some or no unbonded sites, and one or more networks of bond-connected sites. If there are two or more networks of bond-connected sites, then the connectedness of the *hyperpoints* must be supplied by constraint-connections between sites belonging to different networks.

Consider pairs of hyperpoints i and j not directly connected by any $f_{AB}(ij)$. To what extent should absence and presence of $f_R(ij)$ be combined into a bond $e_R(ij)$? Our rule for adopting the combined bond is this:

> *If any site A in i is bond-connected to any site B in j then the combined bond $e_R(ij)$ is adopted.*

This implies the presence of e_R-bonds between all pairs of hyperpoints spanned by a bond-connected network of sites.

Two facts are noteworthy. First, a particular $e_R(ij)$ may be demanded by more than one bond-connected network. Secondly, presence of $e_R(ij)$ and $e_R(ik)$ does not necessarily imply presence of $e_R(jk)$. Presence of the first two bonds in the absence of the third occurs in the following situation. In i, α is the set of sites bond-connected to sites in j, and β is the set of sites bond-connected to sites in k. The sets α and β are disjoint, and no site in j is bond connected to a site in k. An example is shown in Fig. 2.

As in I, the e_R-bonds are treated as legitimate bonds, never to be broken down by $e_R = f_R + 1$. As a result, all hyperpoints spanned by a bond-connected network are irreducibly connected. In the case of a *single* attraction site, analyzed in I, all graphs in $\{S\}$ contain only one bond-connected network, and are rendered irreducible by the process of "filling with e_R bonds." For the case of multiple sites, this is no longer true. We may have a point k where two or more subgraphs are connected purely by constraint connection. No combined e_R-bonds are adopted between hyperpoints in different subgraphs. In the absence of additional f_R-bonds, k remains an articulation point (AP).

We define: for a graph in $\{S\}$ a hyperpoint i is a constraint-articulation point (c-AP) if deleting the constraint connection at i (without deleting any sites or bonds) and disarticulating any incident bonds $f_R(ij)$ or $e_R(ij)$ at i causes the graph to split into two or more connected, but not

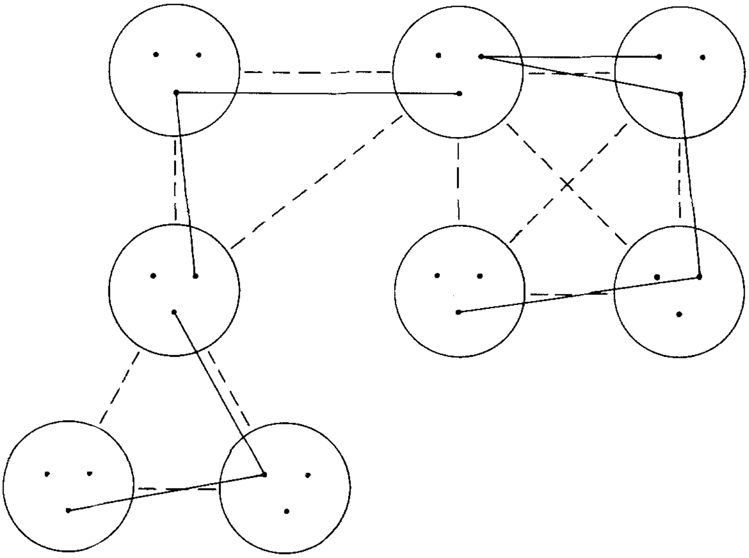

Fig. 2. Filling with e_R-bonds for groups of hyperpoints spanned by bond-connected networks of sites.

mutually connected fragments. In counting fragments, unbonded sites in i are ignored. In other words, the sites α_k in the kth fragment must be bonded to at least one site in another hyperpoint. If M is the number of fragments, and α_0 is the set of unbonded sites, then we have rather trivially, with $M \geqslant 2$,

$$\sum_{k=0}^{M} \alpha_k = \Gamma, \qquad \alpha_i \cap \alpha_j = \varnothing \quad \text{for } i \neq j \tag{8}$$

We can now characterize the graph sum $\{S\}$, for which we borrow the terminology *s-mer graphs* from I. It is convenient to first single out the subclass $\{B\}$ of graphs without f_R-bonds. We name $\{B\}$ the *bare s-mer* graphs.

$\{B\}$ consists of all connected graphs such that the only connectors are f_{AB}-bonds and e_R-bonds between all pairs of hyperpoints which contain mutually bond-connected sites. $\{B\}$ contains both irreducible graphs, and trees of irreducible graphs connected at c-AP's.

We name the set of graphs $\{H\} = \{S\} - \{B\}$ the *hindered* s-mer graphs. The graphs in $\{H\}$ are obtained from the graphs in $\{B\}$ by taking all ways of adding f_R-bonds between pairs of hyperpoints not directly connected by e_R-bonds. $\{H\}$, too, contains both irreducible graphs, and trees of irreducible graphs connected at c-AP's.

Physically, the hindered s-mer graphs take into account steric self-hindrance of bonded s-meric structures, thus correcting for the absence of self-hindrance in the bare s-mer graphs.

Finally, we can express the set of all connected graphs in terms of the graphs in the subclass $\{S\}$ and the monomer hyperpoints:

$\beta pV =$ sum of all connected graphs consisting of s-mer graphs, with $s = 1, 2, \ldots, \infty$, and f_R-bonds between hyperpoints in distinct s-mers. The single hyperpoint without bonds is included.

Here s denotes the number of hyperpoints of an s-mer. Note that the monomers, hyperpoints with all sites unbonded, are included as $s = 1$. The rule for obtaining $\rho(1)$ is unchanged:

$\rho(1) =$ all graphs obtained from βpV by taking all ways of turning a field hyperpoint into a hyperpoint labeled 1.

4. STERIC INCOMPATIBILITY

At least three types of steric incompatibility (SI) can produce useful simplification by making certain graphs exactly zero or negligible. In some but not all cases bond rearrangement of the type carried out in the preceding section is required to make the physical effect of SI manifest in graphical form. Two of the types of SI depend on the presence of more than one attraction site.

The first type, SI1, involves three molecules, but only one site per molecule. It is the same as the sole type of SI encountered in I. When a pair of attraction sites $A(1)$ and $B(2)$ get sufficiently close so that $f_{AB}(12)$ is non-negligible, i.e., when they form a bond, then the repulsive cores of 1, 2, and 3 prevent any site of 3 from coming close enough to $A(1)$ or $B(2)$ to form a bond. This precludes bonding of a site to more than one molecule. In graphical form, SI1 is brought into usable form by the process of filling with e_R-bonds, which kills bonding of $A(1)$ to two hyperpoints 2 and 3 by the presence of the combined bond $e_R(23)$, which is zero for hard core overlap.

The second type, SI2, occurs for molecules with multiple attraction sites. It involves only pairs of molecules. As an example consider hard spheres with two embedded sites, as shown in Fig. 3. Bonded configurations for two such molecules involve only *one* site in 1 and *one* site in 2 for large bond angle θ. For sufficiently small θ, a double bond can be formed: $A(1)$ to $B(2)$, and $B(1)$ to $A(2)$. Except for the unrealistic case of very small θ, multiple bonding of a site is forbidden. We refer to the prohibition of multiple bonding of a site as the weak form, SI2W, and the prohibition of multiple bonding between hyperpoints as the strong form, SI2S of this type of SI.

Whenever SI1 and SI2W both hold exactly or to good approximation, then the *single-bonding condition* applies:

All graphs with multiple bonding of an attraction site are omitted.

In other words, the only surviving bond-connected networks of sites consist of only two sites connected by an attraction bond.

The single bonding condition is easy to apply, produces vast simplification, and underlies all approximation theories discussed in IV. It is physically motivated, because it applies whenever the potential model is

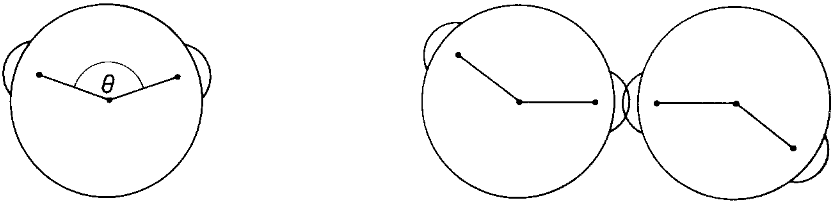

Fig. 3. To the left, model molecule with two attraction sites. The large circle indicates the hard core. The radius of the small circular arcs is half the range of the attraction. To the right a bonded configuration of two such molecules.

tailored to imitate the saturation of the chemical bond that occurs with binding.

The regrouping effected by adoption of the combined e_R-bond insures that incompatible bond configurations which are killed by SI1 stay together when topological reduction is used to eliminate articulation points. This allows us to carry out the reduction in all generality without forgoing the chance to apply the single bonding condition later. Without the regrouping, this would not be the case.

Having motivated the adoption of the combined bond e_R to fill bond-connected networks of sites, it is still necessary to indicate why the filling was not pushed farther. It will emerge that the reason is closely related to yet another type of SI.

Addition of e_R-bonds between hyperpoints without direct connection by attraction bonds produces more highly connected graphs. This reduces the possibilities for including graphs in solutions of integral equations, which generate graphs by composition of subgraphs which share one labeled hyperpoint (use of equation of Ornstein–Zernike type) or two labeled hyperpoints (use of closure equations). For this reason the amalgamation of graphs produced by filling with e_R-bonds is desirable only when negligible graphs are produced by adding graphs that are non-negligible, almost equal, and of opposite sign, or at worst already negligible.

Consider the graphs that survive when the single bonding condition has been applied. An example of such a graph without f_R-bonds is shown in Fig. 4, which also exhibits the chain tetrameric configuration for which it is non-negligible, assuming the molecules to be of the type shown in Fig. 3, with $\theta = \pi$. The combination of hard cores and very short-ranged attractions results in a rather rigid chain. If we add any one of the three possible f_R-bonds, namely, $f_R(13)$, $f_R(24)$, or $f_R(14)$, then we produce a vanishing

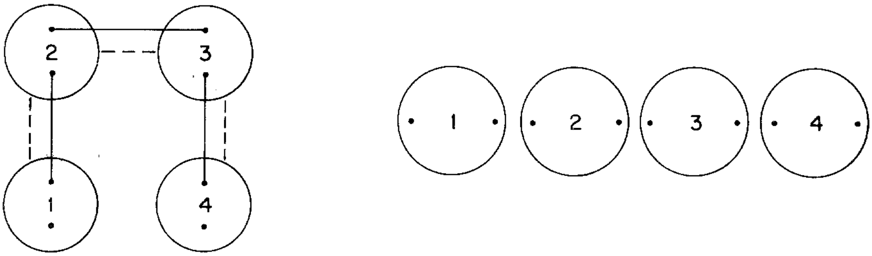

Fig. 4. Illustration of SI3. The graph shown at left is nonvanishing for the chain tetrameric configuration shown at the right. Addition of any of the allowed f_R-bonds produces a vanishing graph.

graph because the core overlap demanded by the f_R-bond is incompatible with the requirement of neither breaking an attraction bond nor violating the core exclusions.

This example is typical of SI3, the last type of SI considered here. It occurs when added f_R-bonds are incompatible with an s-meric structure. Physically, it amounts to the absence of steric self-hindrance which occurs when the rigidity of an s-meric structure prevents two of its component molecules from encountering each other. The extent to which it occurs depends critically on the range of the attractive interactions and the bond angles. For this reason it is harder to incorporate in approximation theories than the other two types of SI.

Clearly, filling with e_R-bonds would be totally counterproductive in the case of the third type of SI, where f_R-bonds rather than e_R-bonds are incompatible with networks of constraints and attraction bonds. This fully justifies the restriction of the filling process to pairs of hyperpoints spanned by a bond-connected networks of sites.

5. DENSITIES AND SUBSIDIARY CONDITIONS

Having explored the physical motivation for the bond-combining rule, we can now return to the next task, the analysis of $\rho(1)$ into several density parameters. For this process, $\rho(1)$ is expressed in the final form attained at the end of Section 3. All graphs are retained; i.e., the possible approximations discussed in Section 4 are *not* assumed.

We are not free to choose the density parameters that appear; they are determined completely by the analysis of connectivity at the labeled point 1. The process of filling with e_R-bonds has eliminated all articulation points such that disarticulation can break a bond-connected network of sites. It will emerge that this results in physically sensible density parameters.

5.1. Definition and Analysis of Densities

We analyze the graphs in $\rho(1)$ in terms of the bonding at the labeled point 1. If α is the set of all bonded attraction sites at 1, then the graph is assigned to $\rho_\alpha(1)$. Clearly, the $\rho_\alpha(1)$ satisfy

$$\rho(1) = \sum_{\alpha \subset \Gamma} \rho_\alpha(1) \tag{9}$$

The sum includes $\rho_0(1)$, representing graphs with no bonded sites at 1. The symbol $\subset$ is defined to include the improper subset $\alpha = \Gamma$.

For each $\rho_\alpha(1)$, we analyze the connectivity of its graphs at the labeled point 1. By a familiar theorem, the graphs in $\rho_0(1)/z$ are the exponential of the subset of graphs for which 1 is not an AP. This expressed by

$$\ln[\rho_0(1)/z] = c_0(1) \tag{10}$$

The graph sum $\rho_\alpha(1)$, with $\alpha \neq \varnothing$, contains the graph sum $\rho_0(1)$ as a factor. The quotient $\rho_\alpha(1)/\rho_0(1)$ contains graphs such that 1 is not a c-AP. These graphs are assigned to $c_\alpha(1)$. In addition there are all graphs such that 1 is a c-AP. These graphs are products of graphs in the $c_\gamma(1)$, where the γ's are a partition of α into nonempty subsets. Thus we have

$$\rho_\alpha(1) = \rho_0(1) \sum_{P(\alpha)=\{\gamma\}} \prod_\gamma c_\gamma(1) \tag{11}$$

where $P(\alpha) = \{\gamma\}$ denotes partition of α into subsets with index γ. The improper partition of a single set $\gamma = \alpha$ is included.

The presence of a labeled point in the $c_\alpha(1)$ makes it easy to carry out the reduction to irreducible graphs, defined as graphs free of AP's. Each $c_\alpha(1)$ contains a subset of irreducible z-graphs. The set of all z-graphs in $c_\alpha(1)$ is obtained by treating the irreducible graphs in the following way. At each field point i add on nothing, or any allowable graph with one labeled point i, which is then turned into a field point. If the set of bonded sites in the irreducible graph is $\alpha(i)$, then the allowable decorations consist of graphs with one LP labeled point i, with sites in α *not* bonded. These are the graphs in $\rho_\gamma(i)$, where γ is $\Gamma - \alpha$ or any subset thereof. We define a set of density parameters $\sigma_\alpha(1)$ by

$$\sigma_\alpha(1) = \sum_{\gamma \subset \alpha} \rho_\gamma(1) \tag{12}$$

and note the special cases

$$\sigma_0(1) = \rho_0(1), \qquad \sigma_\Gamma(1) = \rho(1) \tag{13}$$

Then the rule for expressing the $c_\alpha(1)$ in terms of irreducible graphs contains the following fundamental rule:

> With each field hyperpoint of an irreducible graph we associate a factor $\sigma_{\Gamma-\alpha}(i)$ where α is the set of bonded sites at i. (14)

We have now expressed the $c_\alpha(1)$ as sets of all irreducible graphs with one labeled point. They can all be derived from the fundamental graph sum $c^{(0)}$, defined by the following:

$c^{(0)}$ = sum of all irreducible graphs consisting of s-mer graphs (including monomer hyperpoints) and f_R-bonds. All hyperpoints are field points and carry σ-factors according to the rule (14).

The $c_\alpha(1)$ are obtained from $c^{(0)}$ by the functional differentiation process

$$c_\alpha(1) = \partial c^{(0)}/\partial \sigma_{\Gamma-\alpha}(1) \tag{15}$$

which is equivalent to taking all ways of turning a field point for which α is the set of bonded sites into a hyperpoint labeled 1 and deleting the factor $\sigma_{\Gamma-\alpha}(1)$.

5.2. Algebra of Site Operators

At this point it is convenient to introduce an algebra of site operators; this permits us to carry out further manipulations in very compact and general form. This is accomplished by obviating the need to keep track of the combinatorial conditions that arise from the conditions requiring disjoint sets of bonded sites when subgraphs and/or σ-factors are composed at a point. Examples are seen in (11) and (14).

With each site A at a labeled point i we associate a site operator $\varepsilon_A(i)$. All site operators commute and satisfy

$$\varepsilon_A^2(i) = 0 \tag{16}$$

For products of distinct $\varepsilon_A(i)$ we use the shorthand

$$\varepsilon_\alpha(i) = \prod_{A \in \alpha} \varepsilon_A(i) \tag{17}$$

Let us temporarily suppress the index i, and consider numbers of the form

$$\mathring{x} = x_0 + \sum_{\substack{\alpha \subset \Gamma \\ \alpha \neq \varnothing}} x_\alpha \varepsilon_\alpha \tag{18}$$

They form an algebra which is a straightforward generalization of Clifford's dual numbers, which represent the case of only a single ε. The usual rules of arithmetic and algebra for real numbers also apply to the $\mathring{x}$. The sole exception is this: division by a number with $x_0 = 0$ is forbidden. Analytic functions of $\mathring{x}$ are defined by suitable power series, which terminate with the linear term if we expand in powers of $\mathring{x} - x_0$. In particular, we note

$$(1+\varepsilon)^{-1} = 1 - \varepsilon, \qquad \ln(1 \pm \varepsilon) = \pm\varepsilon \tag{19}$$

Finally, it is useful to adopt the angular brackets $\langle\ \rangle$ as a symbol which instructs us to take the coefficient of ε_Γ of whatever is enclosed. Thus, if $\mathring{x}$ and $\mathring{y}$ are operators of the form (18), then

$$\langle \mathring{x} \rangle = x_\Gamma, \qquad \langle \mathring{y} \rangle = y_\Gamma, \qquad \langle \mathring{x}\mathring{y} \rangle = \sum_{\alpha \subset \Gamma} x_\alpha y_{\Gamma-\alpha} \tag{20}$$

Site operators for different labeled points are independent. When there is more than one labeled point, then subscripts on $\langle\ \rangle$ identify the points i for which reduction to the coefficient of $\varepsilon_\Gamma(i)$ is to be made.

5.3. Conditions in Operator Form

For the one-point quantities $\rho_\alpha(1)$, $\sigma_\alpha(1)$, and $c_\alpha(1)$ we form operator quantities of the form (18), as illustrated for the $\rho_\alpha(1)$:

$$\mathring{\rho}(1) = \rho_0(1) + \sum_{\substack{\alpha \subset \Gamma \\ \alpha \neq \varnothing}} \rho_\alpha(1)\, \varepsilon_\alpha(1) \tag{21}$$

Equation (12) for the $\sigma_\alpha(1)$ in terms of $\rho_\alpha(1)$ becomes

$$\mathring{\sigma}(1) = \mathring{\rho}(1) \prod_{A \in \Gamma} [1 + \varepsilon_A(1)] \tag{22}$$

By use of (19), the inverse is found immediately to be

$$\mathring{\rho}(1) = \mathring{\sigma}(1) \prod_{A \in \Gamma} [1 - \varepsilon_A(1)] \tag{23}$$

which in component form reads

$$\rho_\alpha(1) = \sum_{\gamma \subset \alpha} (-1)^{n(\alpha-\gamma)} \sigma_\gamma(1) \tag{24}$$

where $n(\alpha)$ stands for the number of sites in α.

Similarly, (11) in operator form reads

$$\mathring{\rho}(1)/\rho_0(1) = \exp[\mathring{c}(1) - c_0(1)] \tag{25}$$

and the inverse relation, which expresses the $c_\alpha(1)$ in terms of the $\rho_\alpha(1)$ or the $\sigma_\alpha(1)$ is

$$\mathring{c}(1) - c_0(1) = \ln \frac{\mathring{\rho}(1)}{\rho_0(1)} = \ln \frac{\mathring{\sigma}(1)}{\sigma_0(1)} - \sum_{A \in \Gamma} \varepsilon_A(1) \tag{26}$$

Series expansion of the logarithm yields the result for $c_\alpha(1)$ in explicit form,

$$c_\alpha(1) = \sum_{P(\alpha) = \{\gamma, M\}} (-1)^M (M-1)! \prod_\gamma \hat{\sigma}_\gamma(1) - \delta_{n(\alpha),1} \tag{27}$$

where $P(\alpha) = \{\gamma, M\}$ indicates the partition of α into M subsets, indexed by γ. The sum includes the improper partition, $M = 1$, $\alpha = \gamma$. The $\mathring{\sigma}_\alpha(1)$ are defined by

$$\mathring{\sigma}_\alpha(1) = \sigma_\alpha(1)/\sigma_0(1) \tag{28}$$

Finally, we note the operator forms of these relations that are obtained when (10) is used to undo the exclusion of $c_0(1)$. In the forward direction, we have

$$\mathring{\rho}(1)/z = \exp[\mathring{c}(1)] \tag{29}$$

which has exactly the same form as the analogous relation in the ordinary single-density formalism, with numbers replaced by operators. We will have occasion to use the inverse relation,

$$\mathring{c}(1) = \ln \frac{\mathring{\rho}(1)}{z} = \ln \frac{\mathring{\sigma}(1)}{z} - \sum_{A \in \Gamma} \varepsilon_A(1) \tag{30}$$

6. STATISTICAL THERMODYNAMICS

We follow the procedure in I by proposing an expression for the pressure of a uniform system, and verifying that it satisfies the thermodynamic requirement

$$\beta(\partial p/\partial \mu) = \bar{\rho} \tag{31}$$

where $\bar{\rho}$ is the number density. We give the suggested expression for the pressure both explicitly and in operator form:

$$\beta p V = \int \left[\rho(1) - \sum_{\alpha \subset \Gamma} \sigma_{\Gamma - \alpha}(1)\, c_\alpha(1) \right] d(1) + c^{(0)} \tag{32}$$

$$\beta p V = \int \langle \mathring{\sigma}(1)[1 - \mathring{c}(1)] \rangle\, d(1) + c^{(0)} \tag{33}$$

We take a variation of (33) and note that (15) implies

$$\delta c^{(0)} = \int \langle \mathring{c}(1)\, \delta\mathring{\sigma}(1) \rangle\, d(1) \tag{34}$$

By taking the variation of (30) and multiplying through by $\mathring{\sigma}(1)$ we obtain

$$\delta\mathring{\sigma}(1) - \mathring{\sigma}(1)\, \delta\mathring{c}(1) = \mathring{\sigma}(1)\delta z/z \tag{35}$$

By applying the $\langle\ \rangle$ operation to (35) and using the result and (34), we obtain

$$V\beta\,\delta p = (\delta z/z)\int \rho(1)\,d(1) \tag{36}$$

which is equivalent to (31).

An expression for the Helmholtz free energy $A = N\mu - pV$ is obtained from (32) by using

$$N\beta\mu = \int \rho(1)\left[\ln\frac{\rho_0(1)}{\Lambda} - c_0(1)\right] d(1) \tag{37}$$

which is a direct consequence of (10). Then we obtain

$$\beta A = \int\left[\rho(1)\ln\frac{\rho_0(1)}{\Lambda} - \rho(1) + \sum_{\substack{\alpha\subset\Gamma\\ \alpha\neq\varnothing}} \sigma_{\Gamma-\alpha}(1)\,c_\alpha(1)\right] d(1) - c^{(0)} \tag{38}$$

Many alternative forms can be obtained by using the subsidiary conditions. The form which exhibits the minimum principle for A most clearly is obtained by using (27) to eliminate the $c_\alpha(1)$ altogether. Adopting the σ's as independent variables throughout, we then have

$$\beta A = \int\left[\sigma_\Gamma(1)\ln\frac{\sigma_0(1)}{\Lambda} + Q(1)\right] d(1) - c^{(0)} \tag{39}$$

where

$$Q(1) = -\sum_{A\in\Gamma} \sigma_{\Gamma-A}(1) + \sigma_0(1) \sum_{P(\Gamma)=\{\gamma,M\geqslant 2\}} (-1)^M (M-2)! \prod_\gamma \hat{\sigma}_\gamma(1) \tag{40}$$

Note that here only proper partitions of Γ into two or more sets are allowed. Therefore, $Q(1)$ does not contain $\sigma_\Gamma(1)$.

Minimization of βA with respect to all the $\sigma_\alpha(1)$ subject to the constraint of a constant total number of particles is expressed by

$$\delta\left[\beta A - \lambda\int \sigma_\Gamma(1)\,d(1)\right] = 0 \tag{41}$$

We carry this out, using the form of βA given by (39) and (40). The minimization with respect to $\sigma_\Gamma(1)$ yields

$$\ln\frac{\sigma_0(1)}{\Lambda} - c_0(1) = \lambda \tag{42}$$

which is the subsidiary condition (10), provided that the Lagrange multiplier λ is identified as

$$\lambda = \beta\mu \tag{43}$$

For $\sigma_\alpha(1)$ with $\alpha \neq \Gamma$, the minimization yields

$$\frac{\partial Q(1)}{\partial \sigma_\alpha(1)} + \frac{\sigma_\Gamma(1)}{\sigma_0(1)}\,\delta_{\alpha,\phi} = c_{\Gamma-\alpha}(1) \tag{44}$$

When the differentiations are carried out, using (40) for $Q(1)$, then (44) reproduces exactly the subsidiary conditions for the $c_\alpha(1)$ with $\alpha \neq \varnothing$, as given in (27).

7. CORRELATION FUNCTIONS

The truncated non-normalized s-particle correlation functions $\hat{\rho}_s(1 \cdots s)$ have expansions in z-graphs. They are obtained by taking the graph sum βpV and applying all ways of turning s points into labeled points $1 \cdots s$. Since (hyper)points are invariant under bond rearrangement, this still holds after the bond-combining adopted in Section 3. Again, AP's can be eliminated by taking the subset of graphs free of AP's and replacing each z with a σ-factor according to the rule (14). This applies to labeled points as well as field points. As a result $\hat{\rho}_s(1 \cdots s)$ may be decomposed by

$$\begin{aligned}\hat{\rho}_s(1 \cdots s) = \sum_{\alpha(1) \subset \Gamma} \sigma_{\alpha(1)}(1) \cdots \sum_{\alpha(s) \subset \Gamma} \sigma_{\alpha(s)}(s) \\ \times\, h_{\Gamma-\alpha(1) \cdots \Gamma-\alpha(s)}(1 \cdots s)\end{aligned} \tag{45}$$

where the subscripts in h indicate the bonded sites at the labeled points $1 \cdots s$.

We can construct an operator $\mathring{h}(1 \cdots s)$ by applying the construction defined in (21) independently to each labeled point. Then (45) can be rewritten compactly as

$$\hat{\rho}_s(1 \cdots s) = \langle \mathring{\sigma}(1) \cdots \mathring{\sigma}(s)\, \mathring{h}(1 \cdots s) \rangle_{1 \cdots s} \tag{46}$$

The graphs in $\mathring{h}(1 \cdots s)$ are free of AP's, but may contain bridge points. The further analysis in terms of connectivity at bridge points introduces as building blocks the graphs free of AP's and bridge points, with specified bonding at the labeled points $1 \cdots s$. These sums of irreducible graphs are obtained from $c^{(0)}$ by taking all ways of turning s

points with specified bonding into labeled points, and deleting the σ-factors. In functional differentiation language, these graph sums are

$$c_{\alpha(1)\cdots\alpha(s)}(1\cdots s)=\frac{\partial c^{(0)}}{\partial\sigma_{\Gamma-\alpha(1)}(1)\cdots\partial\sigma_{\Gamma-\alpha(s)}(s)} \tag{47}$$

They represent analogs of the s-particle direct correlation functions.

The most important case is $s=2$. The analysis of the graphs in $\mathring{h}(12)$ into simple chains of irreducible graphs is formalized by an equation of Ornstein–Zernike type. In its compact operator form it is

$$\mathring{h}(12)-\mathring{c}(12)=\int \langle \mathring{c}(13)\,\mathring{\sigma}(3)\,\mathring{h}(32)\rangle_3\, d(3) \tag{48}$$

8. CONCLUSION

We have derived a formally exact reformulation of the statistical thermodynamics of systems of associating molecules with multiple bonding sites. The theory uses several species of particles; each species represents molecules with a specified set of attraction sites bonded. The multidensity formalism seems physically reasonable and has at least three major advantages. The good graph cancelation due to steric incompatibility between repulsion and attraction is preserved in going from z to several densities, while it is destroyed when a single density is used. The opposite extremes of reduction to a site–site level of description, and of introducing complicated structures with internal degrees of freedom are avoided. Finally, the structural similarity to the one-density version of statistical thermodynamics is pronounced. This is very helpful in suggesting approximation theories. This subject is treated in a companion paper.(14)

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