FIELD THEORETIC MODELS OF LIQUIDS

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As an alternative to viewing a liquid explicitly a disordered collection of particles, molecular configurations can be described in terms of single particle fields such as the density. This lecture considers this alternative perspective -- how the spatial analog of harmonic oscillator models leads to integral equations (e.g., PY, RISM, ...), and how manageable non-linear treatments have led to an understanding of freezing. Nevertheless, puzzling questions remain concerning symmetry breaking and the formation of glasses.

INTRODUCTION

With standard graphics, a beginning student can literally view the microscopic structure of a liquid as produced with a molecular dynamics or Monte Carlo computer simulation. The relative arrangements of atoms are disordered, fluctuating and, therefore, responding to disturbances or probes of liquid structure. Despite its chaotic nature, however, there are many important regularities, and these are best described with the principles of statistical mechanics and correlation functions.

According to statistical mechanics, our observations of a macroscopic system are the result of sampling all states or fluctuations consistent with the constraints imposed by our measurements. With simulations, assuming trajectories ergodic, one may perform the sampling by averaging over many steps of a trajectory. With realistic inter-molecular potentials employed, this procedure is often convenient and accurate. But guidance from analytical approaches are useful too. Indeed, numerically intensive simulations have often proved impractical before the appropriate analytical work illustrated what to expect.
This lecture is concerned with an analytical approach, in particular, a phenomenological description of liquid structure. As we will emphasize, quite a bit of detail can be understood without directly confronting the difficult and system specific problems of intermolecular interactions. Ultimately, of course, quantitative theoretical calculations require accurate models for the interactions between elementary constituents. The field theoretic methods we describe here supplement but not replace such calculations.

**CORRELATION FUNCTIONS**

Suppose we characterize a bulk system by specifying the volume, \( V \), the temperature \( T = (\beta k_B)^{-1} \), and perhaps the chemical potential (if the system is open) or the total number of molecules \( N \) (if the system was closed). If these are the only macroscopic characteristics, the average 1-point functions, or fields, seem rather ordinary. For example, consider the density of sites or atoms at position \( \mathbf{r} \). At a given instant, it is

\[
\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)})
\]

where \( \mathbf{r}_i^{(\alpha)} \) is the location of site \( \alpha \) of molecule \( i \). See Fig. 1 for an illustration. (For a polyatomic system there are several sites; for a simple fluid like liquid argon, however, there is only one site per molecule, and in that case we can omit the Greek sub- and superscripts.) In the absence of any externally applied spatially dependent field, the average of this density is the bulk density,

\[
\langle \rho_\alpha(\mathbf{r}) \rangle = \frac{N}{V} = \rho
\]

It is simply a constant in space and dependent upon macroscopic thermodynamic variables only. Results like this might look boring. The final point of this lecture, however, is that the average behavior of density fields are in fact interesting. To reach that point, it is useful to first consider correlation functions -- simultaneous averages of two 1-point functions -- that are manifestly interesting even for a macroscopically homogeneous system.

At any instant, the density will deviate from its average, and the deviation of one position \( \mathbf{r} \) will affect that at another position \( \mathbf{r}' \). These correlations between activities at different points in space are characterized by correlation functions

\[
\chi_{\alpha \gamma}(\mathbf{r}, \mathbf{r}') = \langle \Delta \rho_\alpha(\mathbf{r}) \Delta \rho_\gamma(\mathbf{r}') \rangle
\]
Fig. 1. Instantaneous configuration of molecules in a liquid. The point $\mathbf{r}_i^{(a)}$ refers to the location of the $a$th atom or interaction site of molecule $i$. The cluster diagram superimposed on the drawing illustrates the physical meaning of a typical term in the integral equation described in the INTEGRAL EQUATION section. In particular, the springs denote intramolecular pair distribution functions. These are the off-diagonal (i.e., $a \neq \gamma$) components of the intramolecular response function, $\omega_{\alpha \gamma}(|r-r'|)$. The diagonal components of the response function are delta functions which are depicted diagrammatically as simple circles.

where $\delta \rho_{\alpha \gamma}(r) = \rho_{\alpha \gamma}(r) - \langle \rho_{\alpha \gamma}(r) \rangle$. Owing to its role in linear response or the functional derivative relationship

$$\delta \rho_{\alpha \gamma}(r') = -k_B T \chi_{\alpha \gamma}(r', r') ,$$  \hspace{1cm} (4)

the density-density correlation function is also properly viewed as a response function. [Here, $\phi_{\alpha}(r)$ is a potential field acting on site $\gamma$.] The derivation of (4) follows directly from the standard equilibrium ensemble distribution laws of statistical mechanics. See, for example, Chandler (1982). According to Eq. (4), large spontaneous fluctuations (the right-hand side) imply large responses to applied disturbances (the left-hand side).

On substituting Eq. (1) into Eq. (4), the response function naturally breaks into two parts. One involves the intramolecular response or pair correlations:

$$\omega_{\alpha \gamma}(|r-r'|) = \langle \delta \phi_{\alpha}(r) - \rho(r') \rangle_{\gamma} \ .$$  \hspace{1cm} (5)

The other part involves the intermolecular pair distribution:

$$\rho \delta_{\alpha \gamma}(|r-r'|) = \frac{1}{\rho} \langle N \delta_{\alpha}(r_1^{(a)} - r_1^{(b)}) \delta_{\gamma}(r_2^{(a)} - r_2^{(b)}) \rangle_{\gamma} \delta_{\gamma}(|r-r'|) + 1 \rangle .$$  \hspace{1cm} (6)

In particular, for a uniform one-component molecular fluid, by partitioning of sums and accounting for the equivalency of different
molecules, you find

\[ \chi_{\alpha Y}(z, z') = \rho \omega_{\alpha Y}(|z-z'|) + \rho^2 h_{\alpha Y}(|z-z'|) \] \hspace{1cm} (7)

In light of Eqs. (4) - (7), we see that the response of sites \( \alpha \) at \( z \) due to a disturbance to sites \( Y \) at \( z' \) occurs to an extent proportional to the conditional probability density that the sites \( \alpha \) are present at \( z \) given that sites \( Y \) are found at \( z' \). These pair distributions are measured by neutron and x-ray scattering. This fact is true because the scattering of x-rays and neutrons are due to interference of radiation coming from pairs of scattering centers.

**INTEGRAL EQUATIONS**

A central problem in liquid state theory is the calculation of these pair correlation functions. One phenomenological way to address the problem is based on a mechanistic view which pictures the pair correlations between atoms on different molecules as arising from all possible simple linear sequences of intramolecular and direct intermolecular pair correlations. We will use the notation \( c_{\alpha Y}(|z-z'|) \) to denote this direct correlation or coupling function. With diagrams, the idea is expressed as

\[ \rho^2 h_{\alpha Y}(|z-z'|) = \sum_{\alpha, \gamma} \int dz'' \int dz''' \rho \omega_{\alpha \gamma}(|z-z'|) c_{\eta \lambda}(|z''-z'''|) \]

\[ \times \chi_{\lambda Y}(|z'''-z'|) \] \hspace{1cm} (8)

where the last equality makes clear the meaning of the diagrammatic notation (Chandler, 1982; Landanyi and Chandler, 1975; Chandler and Pratt, 1976; Pratt and Chandler, 1977). The second to last equality is the result of summing all the chains depicted in the first equality. The reader can verify this fact by expanding the second equality via iterative solution employing

\[ \chi_{\alpha Y} = \sum_{\alpha} \chi_{\alpha Y} = \sum_{\alpha} \chi_{\alpha Y} + \ldots \] \hspace{1cm} (9)

as the starting point.
Equation (8) is a type of Dyson equation known as the Chandler-Andersen (or RISM -- "reference interaction site method") equation (Chandler, 1982; Chandler and Andersen, 1972). It is a generalization of the Ornstein-Zernike integral equation for simple atomic fluids (Hansen and McDonald, 1986). It is an integral equation which relates the unknown \( h_{aY}(r-r') \) to the equally unknown \( c_{aY}(r-r') \). Indeed, Eq. (8) is essentially a definition of \( c_{aY}(r) \). Another relationship is required to close the equation, and to construct a closure a field theoretic perspective can be suggestive. We turn to such a perspective now.

**EQUIVALENT GAUSSIAN FIELD THEORY**

Here, we focus on one molecule in the liquid, say molecule 1, and regard all the rest as a bath. See Figure 2. To describe the configurational state of the bath or solvent, we use the dynamical density fields, \( \rho_S(r) \). [Roman subscripts rather than Greek labels are used to help distinguish bath sites from those of the solute -- the tagged molecule. In the end, of course, they will all be the same stuff.] In general, the statistical properties of these fields are quite complicated. At the very least, however, they are characterized by their average behavior and their variance in the absence of the solute, \( \chi_{SS}^{-1}(r-r') \). With only this information, we can construct the probability functional

\[
\mathcal{P}[\rho_S(r)] \propto \exp \left\{ \sum_{a,S} \int dr \ c_{aS}(\rho^{(a)}_S - \rho_S) \rho_S(r) \right. \\
- \frac{1}{2} \sum_{s,s'} \int dr \int dr' \Delta \rho_S(r) \chi_{SS}^{-1}(r, r') \Delta \rho_S(r') \chi_{SS}^{-1}(r', r') \right\} \tag{10}
\]

where \( \chi_{SS}^{-1}(r, r') \) is the functional inverse of the solvent response function; i.e.,

\[
\sum_{s,s'} \int dr'' \chi_{SS}^{-1}(r, r'') \chi_{ss'}^{-1}(r'', r') = \delta_{ss'} \delta(r-r') . \tag{11}
\]

The second part to the right-hand side of Eq. (10) provides a Gaussian distribution for the solvent, and the first part is a linear coupling between the solvent and solute sites.

In the linear coupling term, the coupling function, \( c_{aS}(r) \), is in fact the very same function introduced in Eq. (8). To understand this fact, we can use Eq. (10) to perform the appropriate averages that
Fig. 2. One molecule in a bath. The instantaneous configuration of the bath can be specified by listing the particle coordinates, \([r_1^0, \ldots, r_n^0]\), or equivalently the occupation numbers for positions in space -- the infinitesimal cells illustrated schematically with the grid. To within a factor of the volume element, the occupation numbers are the density fields, \(\rho_g(r)\).

determine \(n_{\alpha g}(r)\). First note

\[
\rho_{\alpha g}(|r-r'|) = \langle \delta(r-r'(\alpha))\rho_g(r)-\rho \rangle
\]

(12)

where we make no distinction between \(\langle \rho_g(r) \rangle\) and \(\rho\). [There would be a difference in a multicomponent system -- a detail the reader can study as an exercise.] Thus

\[
\rho_{\alpha g}^2(|r-r'|) = \int s(r_1^{(1)}, \ldots, r_1^{(n)}) \prod_{\alpha=1}^n dr_1^{(\alpha)} \oint \partial \rho_g(r) P[\rho_g(r)]
\]

\[
\times \delta(r-r'(\alpha)) \rho_g(r') - \rho
\]

(13)

where \(s(r_1^{(1)}, \ldots)\) is the intramolecular distribution for the tagged molecule. The functional integration over the density fields means that one is to integrate \(\rho_g(r)\) over all possible values of density for each point in space. Here, for visualization, one can imagine dividing space into a grid of cells as is illustrated in Fig. 2; \(r\) is then the cell label; and the density, \(\rho_g(r)\), for each cell is to be integrated. In the continuum limit of small cells, this multivariable integration is a functional integration.

The functional integration in Eq. (13) can be performed because \(P[\rho_g(r)]\) is Gaussian. The result of all the integrations is

\[
\rho_{\alpha g}^2(|r-r'|) = \int \cdots \int \rho_g(r)
\]

(14)

Now remember that the solvent is made up of molecules just like the solute. Thus, the \(\chi\)-function on the right-hand side (i.e., the response function represented by the rectangle) is the \(\chi\)-function determined
by \( h_{as}(|r-r'|) \), Eq. (7). Hence, Eq. (14) is the Chandler-Andersen equation (8).

With this model, one may also compute the solvation energy, or more precisely, the excess chemical potential \( \Delta \mu \) for the tagged solute. The calculation is left as an exercise to the reader. The result is

\[
-\beta \Delta \mu = \sum_{a,s} \rho \int dr \ c_{as}(r) + \frac{1}{\langle N \rangle} \int \cdots \int 
\]

\[
= \sum_{a,s} \rho \int dr \ c_{as}(r) 
\]

\[
+ \frac{1}{2} \sum_{a,Y} \sum_{s,s'} \int dr \int dr' \int d(r^{(a)} - r^{(Y)}) \omega_{aY}(|r^{(a)} - r^{(Y)}|) 
\]

\[
\times c_{as}(|r^{(a)} - r^{(Y)}|) \chi_{ss'}(|r - r'|) c_{s,Y}(|r' - r^{(Y)}|) 
\]

(15)

where the second equality makes explicit the diagrammatic meaning of the first. As the diagrammatic depiction indicates, the result is that of a "reaction field" theory. In particular, the first term is a mean field contribution, and the second arises from processes in which the solute pushes on the solvent, and the solvent reacts back (i.e., responds) and pushes the solute. There are no further contributions because the solvent is modeled as a Gaussian bath, and Gaussian (or harmonic) baths exhibit no nonlinear responses.

CLOSURES

The discussion presented above suggests that the coupling function is like an effective pair potential (in units of \( -k_B T \)). It's a rather special potential since its use in a Gaussian field theory is supposed to yield pair correlation functions appropriate to liquids where the actual potentials of interactions are very strong and nonlinear. It is perhaps a surprising fact that simple statements about this function can lead to rather satisfactory theories of liquid structure. For example, when considering nonassociated liquids (e.g., carbon tetrachloride, benzene, carbon disulfide, ...), it is reasonable to consider only the effects of packing forces when examining the liquid structure (Chandler et al., 1983). For this purpose, one often adopts hard core models in which the liquid molecules are conceived of as overlapping fused hard spheres. In that case

\[
g_{aY}(r) = 0, \ r < d_{aY}. 
\]

(16)
where \( d_{\alpha \gamma} \) is the distance of closest approach (as prescribed by molecular geometry and van der Waals radii). Further, since the range of direct interaction between neighboring pairs is also determined by this same set of lengths, one is led to the closure

\[
c_{\alpha \gamma}(r) = 0, \ r > d_{\alpha \gamma}. \tag{17}
\]

The task of determining the liquid structure then reduces to finding the \( c_{\alpha \gamma}(r) \) for \( r < d_{\alpha \gamma} \) which makes \( g_{\alpha \gamma}(r) = 0 \) for \( r < d_{\alpha \gamma} \). Once found, the pair correlations are determined for all distances by inverse Fourier transform of

\[
\hat{h}_{\alpha \gamma}(k) = \left[ \hat{\varphi}(k)\hat{\varphi}(k)[1 - \rho_{\alpha \gamma}(k)]^{-1}\hat{\varphi}(k) \right]_{\alpha \gamma} \tag{18}
\]

where the carots denote Fourier transformation. Equation (18) is, as the reader can verify, another way of writing the Chandler-Anderson equation (8).

This approach is called the RISM theory. Tens of applications of this theory for many different liquids have been quite successful. Representative applications by several workers are found in Trans. Faraday Soc. Discussion (1978). Chandler (1978 and 1982) has reviewed some of this work. Specific examples are Lowden and Chandler (1974), Hsu et al. (1976) and Hsu and Chandler (1978). In its simplest version, that is, when it is applied to single site spherical particles, the RISM theory for hard core molecules reduces to the Percus-Yevick theory for the hard sphere fluid.

Extensions to polar and associated liquids employ different closures. These theories are called "extended RISM." The hypernetted chain closure (HNC) is most often applied (Rossky, 1985), and with reasonable success. See, for example, Pettitt and Rossky (1982), Chiles and Rossky (1984), and Pettitt and Rossky (1986). But this choice of closure is perhaps unnecessarily ad hoc, and others have been suggested (Chandler et al., 1986b).

DENSITY FUNCTIONAL THEORY AND SYMMETRY BREAKING

The pair correlations between atoms or sites in a molecular fluid pertain to the microscopic spontaneous fluctuations that occur in a macroscopically homogeneous fluid. Under certain circumstances, these fluctuations conspire collectively or in concert to form ordered phases such as crystals. The description of these transformations of phase is beyond the scope of the linear (i.e., Gaussian) theory we have outlined thus far. The incorporation of nonlinearities is the subject we turn to
now. The methodology we consider is known as density functional theory.

For simple atomic fluids and solids, this remarkable formulation of equilibrium statistical mechanics was pioneered more than 20 years ago. See, for example, Morita and Hiroike (1961), Stillinger and Buff (1962) and Lebowitz and Percus (1963). The formulation rests on a variational principle enunciated by Morita and Hiroike (1961):

\[ \delta \bar{F} / \delta \rho(r) \ldots \delta \rho(r') \] generates all correlation functions, and \[ F[\rho(r)] \] is the minimum of \[ F[\rho(r)] \] on the surface \[ \int d\rho(r) = \langle N \rangle. \]

This principle can be viewed as a microscopic version of thermodynamics. It says that the computation of correlation functions is equivalent to identifying \[ F[\rho(r)] \] and determining the density field which minimizes that functional. Notice too that it says all statistical information of the equilibrium state (i.e., all multipoint correlation functions) is contained in the reversible work functional for the 1-point density field. It's such an important result, it should cause all but the most casual reader to pause.

It is convenient to separate this free energy functional into two parts:

\[ F[\rho(r)] = F_0[\rho(r)] + F_1[\rho(r)] \]  \hspace{1cm} (19)

where \( F_0[\rho(r)] \) is the free energy functional for the case where different particles did not interact with one another, and \( F_1[\rho(r)] \) is the correction to that ideal gas expression. One may show that (Morita and Hiroike, 1961)

\[ F_0[\rho(r)] = \int d\rho(\rho(r)) \Delta \rho(r) \Delta \rho(r') - 1 \]  \hspace{1cm} (20)

which has the physical interpretation of an entropy of mixing. Further, the interaction contribution can be expressed formally as (Morita and Hiroike, 1961; Stillinger and Buff, 1962),

\[ F_1[\rho(r)] = - \frac{1}{2} \int d\rho / d\rho' \bar{C}[r,r';\rho(r)] \Delta \rho(r) \Delta \rho(r') \]  \hspace{1cm} (21)

where \( \Delta \rho(r) \) is the deviation in density from that of a convenient reference state. If we assume the free energy is analytic, the coupling functional, \( \bar{C}[r,r';\rho(r)] \), can be expanded about that of the reference state. To lowest order when the reference state is a homogeneous fluid of density \( \rho \), one finds
Fig. 3. Free energy functionals of density fields. Case (a) is monostable, i.e. $\delta F/\delta \rho(r)$ possesses only one solution, and a linear theory can describe the region close to the minimum. Case (b) shows two stable or metastable phases characterized by different average density fields. When two phases are in equilibrium, the value of $\Delta F$ in Case (b) coincides with equality of the grand canonical free energy for the two stable states.

$$\bar{\sigma}[\rho(r); \rho(r')] = \sigma(|r-r'|; \rho)$$  \hspace{1cm} (22)

where $\sigma(r)$ is the direct correlation function. In other words,

$$[\delta^2 F/\delta \rho(r) \delta \rho(r')]_{\text{uniform}} = \frac{1}{\rho} \delta(r-r') - \sigma(|r-r'|)$$

$$= \chi^{-1}(|r-r'|).$$  \hspace{1cm} (23)

In the second equality we are identifying the connection between the direct correlation function and the functional inverse of the response function for a uniform simple atomic fluid. The reader can verify this result using the Ornstein-Zernike equation [i.e., the Chandler-Andersen equation (8) for an atomic or single site fluid] and Eq. (11). As $\rho(r) \rightarrow \rho$, Eq. (22) becomes exact. Its use for all $\rho(r)$, however, is an approximation -- the hypernetted chain approximation.

In a harmonic approximation, $F[\rho(r)]$ is a quadratic functional with its minimum at $\rho(r) = \rho$ and its curvature given by $\chi^{-1}(|r-r'|)$. The minimization principle, $\delta F/\delta \rho(r) = 0$, is a linear equation with only one solution, $\rho(r) = \rho$. See Fig. 3. One way to construct a nonlinear density field theory where $F[\rho(r)]$ may have more than one minimum is to use without approximation the $\rho^2 \rho$ term, Eq. (20), but to approximate the coupling functional as done in Eq. (22). This approximation for the free energy functional has been successfully applied as a theory for freezing of simple fluids (Ramakrishnan and Yussouff, 1979). That is, with Eqs. (19)-(22), $\delta F/\delta \rho(r)$ = 0 is a nonlinear equation with multiple solutions; and the crystalline solutions of broken symmetry accurately describe the freezing of atomic fluids (Haymet, 1987). Since this theory relies on a truncated Taylor expansion to estimate $F_1$, the theory is a type of "Landau theory" or "mean field theory." In other words, one assumes
analyticity of the free energy functional in the vicinity of a phase transition.

In implementing the theory, one requires information about the interparticle potentials only as it appears implicitly through \( c(|r-r'|) \) or equivalently the pair correlation function of the dense homogeneous fluid. The fact that this simple approach which requires only information about the homogeneous system actually succeeds at explaining the freezing of, for example, liquid argon deserves some comment. In particular, one should note that \( F[\rho(r)] \) is the reversible work function for changing density fields. By employing Eq. (22), one assumes a relatively small change in the interparticle interaction contribution to the work when changing \( \rho(r) \) from that of a dense fluid to that of a solid. This assumption seems reasonable since the nearest neighbor environment of a particle in a dense fluid is rather similar to that in a solid. Nevertheless, subtle changes in that environment can have a more pronounced and collective effect on the entropy term. For this reason, it is important to retain the nonlinear structure of Eq. (20).

DENSITY FUNCTIONAL THEORY OF POLYATOMICS

Non-simple molecular fluids and solids can also be analyzed with density functional theory. Here, the trick is to regard molecules as objects composed of atoms. (An alternative view in which molecules are made up of spherical harmonics is possible, but then the density fields involve orientational variables as well as points in space.) With the atomistic view of molecules, as we have illustrated in the first part of this lecture, one can use the site or atomic density fields, \( \rho_a(r) \), to describe configurational states. Furthermore, the following generalization of atomic density functional theory has been derived (Chandler et al., 1986a):

There exists a free energy density functional, \( F[\rho_a(r)] \)

such that \( \delta^n F / \delta \rho_a(r) \ldots \delta \rho_a(r') \) generates all correlation functions, and \( F[\{\rho_a(r)\}] \) is the minimum of \( F[\rho_a(r)] \)
on the surface \( \langle N \rangle = \int dr \rho_a(r) \).

Notice again the remarkable nature of this result. It implies that all information is contained in the 1-point density fields and the variation of the free energy with those fields. As with the atomic case, one may write

\[
F[\rho_a(r)] = F_0[\rho_a(r)] + F_I[\rho_a(r)]
\]

where

\[
F_I[\rho_a(r)] = \frac{1}{2} \sum_{\alpha, \gamma} \int dr \int dr' \sigma_{a\gamma}[r, r'; \{\rho_a(r)\}] \Delta \rho_a(r) \Delta \rho_a(r')
\]

\( 11 \)
and when expanded about the uniform fluid reference state,

\[
\bar{c}_{a}[(r, r'; \rho_{a}(r))] = \bar{c}_{a}[(r, r'; \rho)] = c_{a}(|r-r'|, \rho) . \tag{26}
\]

The entropy of mixing functional, however, does not have standard \(\rho\) \(\ln \rho\) form. Indeed,

\[
F_{\rho}[[\rho_{a}(r)]] = \sum_{a} \int d\rho_{a}(r) \ln \rho_{a}(r)-1 \] . \tag{27}

For this equality to hold, we would have to imagine that atoms within the same molecule were uncorrelated. The different atoms are, however, bonded; and the configurational constraints imposed by the bonding reduce the mixing entropy from that estimated with the right-hand side of (27). Further, for the physical reasons discussed in the preceding section, we require an accurate treatment of the entropy contribution to understand transformation of phases, spontaneous assemblies and many other symmetry breaking phenomena.

The determination of the entropy of mixing functional with bonding constraints is obtained by introducing an additional set of fields -- "fugacity fields" -- akin to the procedures of Lagrange multipliers in multivariable calculus. The result of this analysis is the set of variational equations

\[
0 = \delta F_{\rho}/\delta z_{a}^{a}(r) \tag{28a}
\]

and

\[
0 = \delta [F_{\rho} + F_{I}]/\delta \rho_{a}(r) \tag{28b}
\]

where

\[
F_{\rho}[[\rho_{a}(r)],[z_{a}(r)]] = \sum_{a=1}^{n} \int d\rho_{a}(r) \ln z_{a}(r) + \int s_{a}(r^{(1)}, ..., r^{(n)}) \prod_{a=1}^{n} z_{a}(r^{(a)}) d\rho_{a}(r) \tag{29}
\]

and \(F_{I} = F_{\rho}[[\rho_{a}(r)]]\) is given by (25) and presumably well approximated with (26). It is evident, as the reader can verify, that the solutions of Eq. (28a) satisfy the bonding constraints as specified by the intramolecular distribution function, \(s_{a}(r^{(1)}, ..., r^{(n)})\).

Equations (25), (26), (28) and (29) have been applied to liquid water to describe the freezing of that system to form ice I\(_h\) (Ding et al., 1987). The calculations required as input the pair correlation functions of the liquid. These were taken from experiment. The theory
predicts a freezing temperature of \(-5^\circ C\) (the experimental result is, of course, \(0^\circ C\)), and a density of the solid as \(0.030\) molecules/\(\text{Å}^3\) (experiment is the same to that number of figures). The theory therefore predicts that ice floats on water; it also predicts a positive coefficient of thermal expansion of the solid in accord with experiment.

THE FUTURE

There are still a number of important problems where the field theoretic approaches we have outlined have yet to be applied successfully. These include the solvation of strongly bound complexes, the formation of glasses and also the phenomenon of liquid crystallinity. In the first of these, the strength of intermolecular bonding may invalidate approximations like Eqs. (22) or (26), and it is not yet clear how to progress beyond that stage. In the second example, one is faced with the phenomenon of nonergodicity, perhaps described by a reversible work functional with a chaotic multiple of deep metastable minima. It is not at all clear that the free energy relevant to stable equilibrium states considered herein is the appropriate functional for the glassy case too. The issues here are also pertinent to fundamental questions about spontaneous symmetry breaking. They are perhaps highlighted by the example of liquid crystallinity. For nematic liquid crystals, translational symmetry of the equilibrium state requires that \(\langle p_a(r) \rangle = p\). Yet, the fundamental principle of density functional theory implies that the set of \(\langle p_a(r) \rangle\)'s contain all information concerning the equilibrium state. Yet the order parameter characterizing a liquid crystal seems absent from the 1-point density fields. The resolution of this apparent paradox resides in the demonstration that the orientational order and broken symmetry of a liquid crystal is contained in objects like \(\langle \sum \mathbf{r}^2 [p_a(r) - p_b(r)] \rangle\), where \(a\) and \(b\) are nonequivalent sites. The demonstration is left as an exercise for the reader.

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