International Journal of Thermophysics, Vol. 10, No. 1, 1989

Theory of Freezing: The Inhomogeneous Ornstein–Zernike Equation[1]

J. D. McCoy[2] and A. D. J. Haymet[2, 3]

We present a new freezing theory based on the inhomogeneous Ornstein–Zernike equation. The new theory is nonperturbative, in the sense that crystal and liquid are treated at the same level of approximation. This is in contrast to the popular density functional theory of freezing, which uses the liquid as a reference state for perturbation theory. Due to the demanding nature of the numerical method, preliminary calculations are presented for a model problem—which, in the strictest sense, is unphysical—namely, the freezing of hard disks in two dimensions. We also explore a generalized Percus–Yevick closure appropriate for the crystal.

KEY WORDS: freezing; hard disks; Ornstein–Zernike equation.

1. INTRODUCTION

This paper introduces a new theory for the freezing of simple liquids. The theory draws upon ideas from bulk liquid theory developed by Lovett et al. [1] and Werthiem [2] and extended very recently by Plischke and Henderson [3–7]. The new freezing theory is labeled "nonperturbative" to distinguish it from the "density functional" theory of freezing [8], which is based on thermodynamic perturbation theory and which has been developed extensively recently [8–34] by us and many other workers.

In summary, the new theory seeks to place the prediction of the structure (and hence the thermodynamics) of ordered crystals (and, in fact, quasiperiodic materials [10]) on the same footing as the structure of liquids, by using integral equations [7] to predict the full position- and

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

[3] Present address: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

0195-928X/89/0100-0087$06.00/0 © 1989 Plenum Publishing Corporation

angle-dependent pair correlation function $g(r_1, r_2)$ of the crystal. From this microscopic structural information, the free energy and other thermodynamic properties of the crystal can be calculated. By comparison with existing integral equation theories for the liquid phase, we intend to predict the stability of the crystal and, hence, the phase diagram.

The formalism of the new theory is stated in Section 2, and preliminary results are presented in Section 3. A proposed modification of the Percus–Yevick closure—in essence, a new integral equation closure appropriate for crystals—is introduced in Section 4, and its numerical properties are explored in Section 5. Our conclusions are collected in Section 6.

It should be emphasized that this theory will not (nor is it intended to) replace the density functional (DF) theory as a practical means of predicting phase diagrams, the crystal/melt interface, and the nucleation of crystals from the melt [8]. It is intended as a more fundamental (but still not exact) theory which avoids one of the two main approximations in DF theory and tests the most radical assumptions in that theory. The importance of freezing cannot be overstated. At low temperatures, the freezing transition is observed in every material, with the possible exception of liquid helium at low pressures. At present there is no first-principles theory that can predict the phase diagram of a given material, even starting from a complete knowledge of the forces between the constituent molecules.

2. THEORY

In theoretical calculations of the microscopic structure of the liquid state, it has proved useful to work with the Ornstein–Zedrnike (OZ) equation. The OZ equation is, in essence, a definition of the direct correlation function $c(r_1, r_2)$ in terms of the pair correlation function $h(r_1, r_2)$ and the singlet density $\rho(r_1)$. The form of this definition is obtained either by partial summation of diagrams or by density functional theory [9]. We adopt the latter approach (although the methods are equivalent).

Calculation of the Fourier transform of the structure factor $\chi(r_1, r_2)$, or a closely related function such as the pair correlation function, is usually the primary objective of a microscopic theory. The direct correlation function often is viewed as no more than a tool to be used in achieving this objective. However, since the direct correlation function is related to the change in the free energy upon variation of the singlet density, its physical significance has been exploited in mean field theories of phase transitions, in which this response of the free energy to a density variation is the crucial question. In addition, this feature is also useful in developing closures, as shown below.

The Fourier transform of the structure factor is an appropriate place to begin a more detailed discussion of the OZ equation. This quantity is the response of $\rho(r_1)$ to a variation in the function $\psi(r_2)$,

$$\frac{\delta\rho(r_1)}{\delta\psi(r_2)}=\chi(r_1, r_2) \tag{1}$$

where $kT\psi(r_2)$ is the chemical potential of the system minus the external field, k is the Boltzmann constant, and T is the temperature. The pair correlation function is defined in terms of the structure factor transform by

$$\chi(r_1, r_2)=\delta(|r_1-r_2|)\,\rho(r_1)+\rho(r_1)\,\rho(r_2)\,h(r_1, r_2) \tag{2}$$

where $\delta(|r_1-r_2|)$ is the Dirac delta function. The singlet density is related to the field $\psi(r_2)$ by a Boltzmann-like expression:

$$\rho(r)=e^{\psi(r)+\tilde{C}(r)} \tag{3}$$

where the deviation of $\rho(r)$ from strictly Boltzmann-like behavior with respect to $\psi(r)$ serves as a definition of the function $\tilde{C}(r)$. Note that the arbitrary constant inherent in the definition of the chemical potential is used to absorb the proportionality constant. The functional derivative of $\psi(r)$ with respect to $\rho(r)$ yields

$$\frac{\delta\psi(r_1)}{\delta\rho(r_2)}=\frac{\delta(r_1-r_2)}{\rho(r_2)}-c(r_1, r_2) \tag{4}$$

where the direct correlation function is defined to be

$$\frac{\delta\tilde{C}(r_1)}{\delta\rho(r_2)}=c(r_1, r_2) \tag{5}$$

Equation (4) is the functional inverse of the structure factor transform $\chi^{-1}(r_1, r_2)$. The OZ equation is a statement of this inverse relationship:

$$\delta(|r_1-r_3|)=\int d^3r_2\,\chi^{-1}(r_1, r_2)\,\chi(r_2, r_3) \tag{6}$$

Upon substitution of Eqs. (2) and (4) into Eq. (6), the OZ equation can be written in its more familiar form:

$$\rho(r_1)\,h(r_1, r_3)=\rho(r_1)\,c(r_1, r_2)+\int d^3r_2\,\rho(r_1)\,c(r_1, r_2)\,\rho(r_2)\,h(r_2, r_3) \tag{7}$$

It may seem that the OZ equation serves only to relate the unknown function $h(r_1, r_2)$ to the equally unknown function $c(r_1, r_2)$. Indeed, the use of the OZ equation makes sense only in conjunction with a second equation—known as a closure—which also relates h and c. In terms of density functional theory, the closure contains the physics of the problem. This problem can be stated simply as the minimization of the grand potential free energy functional $W[\rho(r)]$ with respect to the singlet density:

$$\frac{\delta W}{\delta \rho(r)} = 0 \tag{8}$$

where this minimization is in the presence of an external field which produces a particle centered at a particular location $\bar{r}$ in the system. This "unphysical" field is known as a particle generating (PG) field. The singlet density $\bar{\rho}(r)$ which minimizes $W[\rho(r)]$ can then be interpreted as

$$\bar{\rho}(r) = \rho_0(r)\, g(r, \bar{r}) \tag{9}$$

where $\rho_0(r)$ is the singlet density and $g(r, \bar{r}) = h(r, \bar{r}) + 1$, both in the absence of the PG field. One is not able to attempt an exact treatment of Eq. (8). Rather, an approximate functional form for $W[\rho(r)]$ is introduced, and it is the approximate free energy functional which is minimized. The approximate $W[\rho(r)]$ is usually taken to be

$$\begin{aligned}\beta W = \beta W_0 &+ \int dr\, \rho(r)[\ln(\rho(r)/\rho_0(\mathrm{r})) - 1] + \int dr\, \rho_0(r)\\ &- \int dr\, \rho(r)[\psi(r) - \psi_0(r)] - \tfrac{1}{2}\int dr \int dr'\, c(r, r')\, \Delta\rho(r)\, \Delta\rho(r')\end{aligned} \tag{10}$$

where $\Delta\rho(r) = \rho(r) - \rho_0(r)$, $\beta = 1/kT$, and $\psi(r)$ differs from $\psi_0(r)$ by the PG field. Equation (10) is the result of a functional Taylor series of the Helmholtz free energy in terms of the singlet density followed by Legendre transformation to the grand potential free energy.

The formal minimization of Eq. (10) is

$$0 = \ln[\bar{\rho}(r)/\rho_0(r)] + \beta u(|r - \bar{r}|) - \int dr'\, c(r, r')\, \Delta\bar{\rho}(r) \tag{11}$$

where $u(|r - \bar{r}|)$ is the PG field. Note that any external field which is present both before and after the PG field is applied will not appear in this closure. By substituting the relation (9) for $\bar{\rho}(r)$, and with judicial use of the OZ equation, one finds the familiar hypernetted chain (HNC) closure:

$$0 = \ln g(r, \bar{r}) + \beta u(|r - \bar{r}|) - [h(r, \bar{r}) - c(r, \bar{r})] \tag{12}$$

Upon linearization, the HNC closure produces the equally familiar Percus–Yevick (PY) closure:

$$c(r, \bar{r}) = g(r, \bar{r})[1 - e^{\beta u(|r - \bar{r}|)}] \tag{13}$$

Both the PY and the HNC closure have been used extensively in theories of the liquid state with marked success.

In our current work, we are interested in the solution of the PY equation for the case of nonconstant singlet density with a small or zero external field. Before we discuss the finer details of our calculations, we wish to comment on the applicability of Eq. (9) to the case of nonconstant density. In particular, we consider the limiting case of a symmetry breaking (SB) field. First, a brief digression on the role of the SB field in statistical mechanics is in order. For the case of a crystal without an external field, the singlet density would be found to be a constant if it were possible to solve exactly for the singlet density by way of the partition function. Nothing in the partition function prevents the crystal from drifting through space. Hence, even though the real singlet density is sharply peaked on a short time scale, the average given by the partition function is a long time average and so the density is a constant. The well-known solution to this predicament, due to Kirkwood, is the use of a symmetry breaking field. The symmetry breaking field is an infinitesimally small field located in a specific position in the unit cell. This, in effect, stops the crystal from drifting, and the singlet density given by the exact calculation with the symmetry breaking field is nonconstant.

In the language of this paper, if Eq. (8) could be solved for the exact free energy functional without any external field, a constant singlet density would be found. If a SB field was incorporated into the free energy functional, Eq. (8) would give the singlet density $\rho_0(r)$. Now consider the consequences of adding both a PG and a SB field to the free energy. Our hypothetical exact calculation would produce the exact singlet density for this case $\bar{\rho}(r)$. The one remaining step to obtain the pair correlation function is the use of Eq. (9). The SB field serves to center the singlet densities in the unit cells. Equation (9) implies that a PG field can be located at any point in the unit cell without shifting the singlet densities of the entire crystal. We suspect that this is incorrect. Rather, we believe that the PG field would take on the role of the SB field and Eq. (9) would become

$$\bar{\rho}(r) = \rho_0(r - \bar{r})\, g(r - \bar{r}, 0) \tag{14}$$

for any position $\bar{r}$ of the PG field. That is, the crystal would always be centered about $\bar{r}$ rather than the position indicated by the SB field. If this line of reasoning is correct, one would wish to minimize the free energy in the presence of a PG field but require that the singlet densities be constrained in a manner which localizes the effect of the PG field and does not shift the entire crystal. One check on the self-consistency of the calculation which we consider in the next section is

$$\int_{\Delta} dr\, \rho_0(r)\, g(r, \bar{r})\, \rho_0(\bar{r}) = \rho_0(\bar{r}) \tag{15}$$

where the integration is over any unit cell (of volume Δ) other than the one which contains the PG field and where the densities are normalized to one particle per unit cell. Notice that for the true $\rho_0(r)$ and $g(r, \bar{r})$, Eq. (15) is exact.

3. THE PY CLOSURE: RESULTS

We have performed extensive calculations on two-dimensional systems with periodic order using the PY closure, and we now present here (i) our methodology for treating the numerical difficulties due to the large dimensionality of the two-point functions $h(r, \bar{r})$ and $c(r, \bar{r})$, (ii) selected results of our calculations for systems with Gaussian densities on a triangular lattice and (iii) a comment on the self-consistency of these results in light of Eq. (15).

Consider the OZ equation as written in Eq. (7). There is a temptation at this point to divide through by $\rho(r_1)$; however, due to the sharply peaked nature of the Gaussian densities considered here, it is convenient to retain $\rho(r_1)$ and simply define the new functions:

$$H(r_1, r_2) = \rho(r_1)\, h(r_1, r_2) \tag{16}$$

$$C(r_1, r_2) = \rho(r_1)\, c(r_1, r_2) \tag{17}$$

Substituting these two definitions into Eq. (7) produces the form of the OZ equation which we have used in this work,

$$H(r_1, r_2) = C(r_1, r_2) + \int d^3r_2\, C(r_1, r_2)\, H(r_2, r_3) \tag{18}$$

It may seem that there would be an additional advantage to using functions which are weighted by the densities at both positions, that is, to use

$$H^*(r_1, r_2) = \rho^{1/2}(r_1)\, h(r_1, r_2)\, \rho^{1/2}(r_2) \tag{19}$$

rather than $H(r_1, r_2)$. The nonzero values of $H^*(r_1, r_2)$ and $C^*(r_1, r_2)$ are only for r_1 and r_2 near density peaks, while the nonzero values of $H(r_1, r_2)$ and $C(r_1, r_2)$ exist for r_1 near a density peak and for all r_2. However, the value of $H(r_1, r_2)$ and $C(r_1, r_2)$ is needed only for r_1 and r_2 near density peaks for iteration of the OZ equation. Hence, the definitions of H and C encompass the benefits inherent in the use of H^* and C^* in terms of restricting the necessary domain of the functions. The symmetric nature of H^* and C^* does make programming slightly easier, but the choice of H and C is more in the spirit of the derivation. In either case, the resulting OZ equation has no explicit dependence on the singlet density. Instead, the chosen closure manifests a density dependence which one would not normally expect. In our case, we have used the Percus–Yevick (PY) closure, which is

$$\begin{aligned} H(r_1, r_2) &= -\rho(r_1), && \text{if } |r_1 - r_2| < \sigma \\ C(r_1, r_2) &= 0, && \text{if } |r_1 - r_2| > \sigma \end{aligned} \tag{20}$$

where we have restricted our work to hard disks of diameter σ. We have also restricted the singlet density to Gaussian peaks on a triangular lattice:

$$\rho(r_1) = A(\pi\varepsilon\rho^2)^{-1} \sum_R \exp(-|r_1 - R|^2/\varepsilon^2) \tag{21}$$

where ε is the Gaussian width, A is the average number of particles per unit cell, and R is one of the lattice vectors which depend on the nearest-neighbor separation d.

The primary difficulty in working with nonconstant singlet densities is coping with the large dimensionality of the functions h and c. Even viewing the results is not straight forward; in order to plot h and c one must reduce the dimensionality in a physically meaningful manner. We have used two types of plots in this work. First, one of the coordinates is fixed, say $r_1 = X$, and the function $h(X, r_2)$ or $c(X, r_2)$ is plotted either as a contour or as a mesh plot where r_2 is the variable. Second, a density-weighted average is used to reduce the dimensionality even further. We denote these averages by a subscript a, for example,

$$h_a(r) = \frac{\int dr_1 \int dr_2\, \rho(r_1)\, h(r_1, r_2)\, \rho(r_2)\, \delta(|r_1 - r_2| - r)}{\int dr_1 \int dr_2\, \rho(r_1)\, \rho(r_2)\, \delta(|r_1 - r_2| - r)} \tag{22}$$

Clearly, this average—as well as a number of other possible averages—reduces to the liquid-state average for constant density. We are interested in the specific average $h_a(r)$ because this function is related to the scattering intensity in experimental work. We have also examined the density-weighted direct correlation function $c_a(r)$, although it is not clear that it has physical significance. In any case, $c_a(r)$ is not related to the functional inverse of $h_a(r)$ in the same way that $c(r_1, r_2)$ is related to the inverse of $h(r_1, r_2)$—except, of course, in the case of constant density.

The application of the above equations is extremely computer intensive. We have used a coarse grid size and integrated over only the nearest-neighbor unit cells in an attempt to make the run times involved manageable. We used a grid of 90 points chosen in each unit cell at a distance of no more than 0.25σ from the center of the cell. (The short-ranged nature of H and C permit us to truncate at such short distances.) One may think that a much larger number of points would be easy to incorporate; however, even at 90 points, we must keep track of 16,200 values of the two-point functions. As a result, the convolution in the OZ equation involves of the order of 10^8 terms. To date we have attempted only Picard iteration procedures. The solutions were started with densities of small A and A was increased as far as 1.

Our preliminary results seem to indicate that the direct correlation function—as defined above—diverges near $A = 0.9$. In Fig. 1 the pressure P_c (calculated from the compressibility equation and hence the direct correlation function) is plotted as a function of A for $d = 1.10318\sigma$ and $\varepsilon = 0.088\sigma$. Although the direct correlation function seems to diverge, the

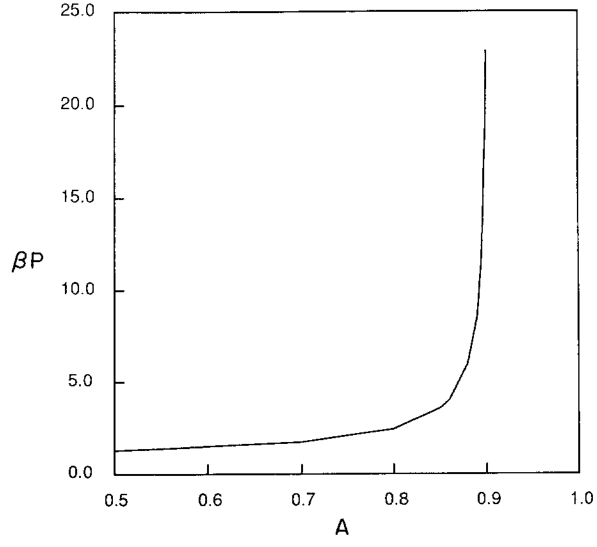

Fig. 1. The reduced pressure βP (in units of σ^{-2}) calculated from the compressibility equation as a function of the number of particles per unit cell A.

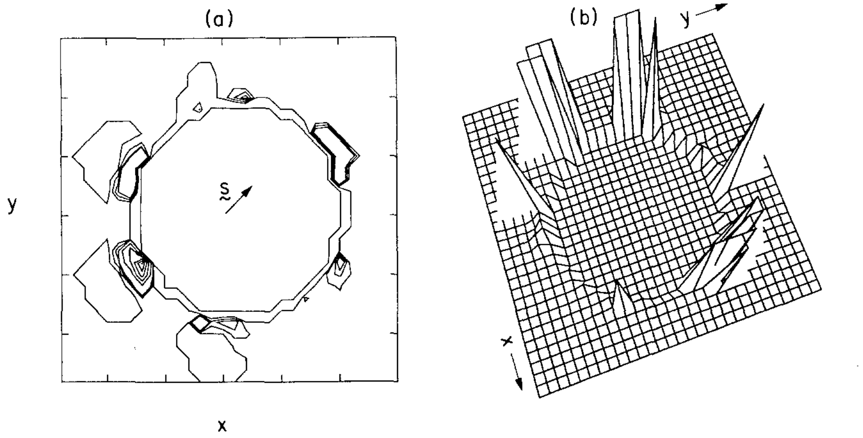

Fig. 2. The pair correlation function $h(s, r)$ for fixed s, for $\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, and $A = 0.90$. (a) Contour plot of $h(s, r)$. The center of the unit cell of the center unit cell is located in the center of the plot. The point s is toward the upper right corner as shown, and as a consequence, the large $h(s, r) = -1$ area is to be centered on s. One can see traces of each of the six neighboring cells. (b) Mesh plot of $h(s, r)$. The large peaks at the left have been clipped to 20% of their peak value. Notice that these back correlations are larger than the correlations in the s direction.

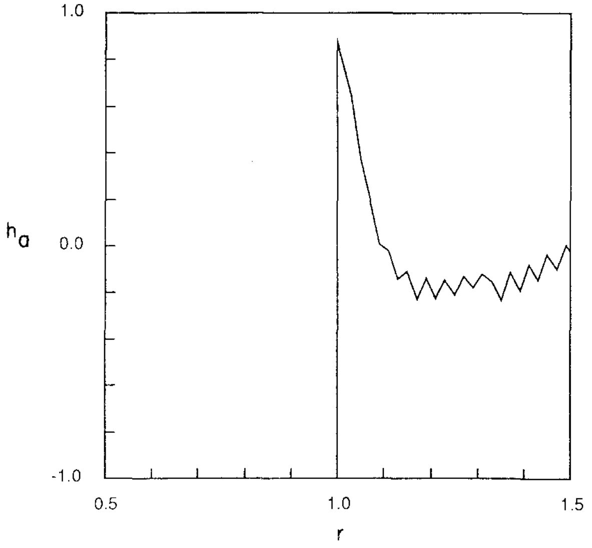

Fig. 3. The density-weighted pair correlation function h_a for $\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, and $A = 0.90$ (r in units of σ).

pair correlation function does not. In the case of large separation of the unit cells, we were able to recover the solution after the divergence and, consequently, to increase A to the value of 1. For the case of $d = 1.10318\sigma$, we were able to track the solution only until the divergence. In Fig. 2, we show the function $h(s, r)$ for the case ($\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, $A = 0.9$), where s is displaced from the center in the unit cell. In Fig. 3 the density-weighted average is shown for the same case.

There are several possible reasons for the violation of the consistency relation (15): (i) fundamental problems with the use of Eq. (9) for non-constant densities, (ii) the form of the approximate free energy [Eq. (10)], and (iii) the large grid used in our numerical calculations. The deviations are rather systematic for the latter to be the sole reason.

4. A NEW, CONSTRAINED, PY CLOSURE

Our preliminary numerical results, presented above, suggest that the self-consistency condition [Eq. (15)] may not hold for solutions of the PY closure in a two-dimensional hard disk system with Gaussian singlet densities. This feature is still under investigation. In this section we propose a new closure which embodies Eq. (15) as a constraint.

From Eq. (9), we formulate a set of constraints

$$\int_{\Delta + \bar{R}} dr\, \bar{\rho}(r \mid R) - A = 0 \tag{23}$$

where $\Delta + \bar{R}$ indicates that the integration is over the unit cell located at lattice vector $\bar{R}$, $\rho_0(r)$ is generalized to normalize the number of particles per unit cell to A, and $\bar{\rho}(r \mid R)$ denotes the singlet density in the cell located at R. The functional to be minimized with the constraints is

$$\beta W^* = \beta W + \sum_{R = \bar{R}} \lambda_{\bar{r}\bar{R}}(R) \left[\int_{\Delta + R} dr\, \rho(r \mid R) - A \right] \tag{24}$$

where the PG field is located at $\bar{r}$ in the located at $\bar{R}$. The minimization of W^* with respect to the undetermined multipliers $\lambda_{\bar{r}\bar{R}}(R)$ enforces the constraints (23). Note that each position of the PG field gives a new set of λ's (the subscripts $\bar{r}$ and $\bar{R}$) and that, in addition, each integrated cell has a different λ (the variable R). The minimization of W^* with respect to $\rho(r \mid R)$ gives

$$0 = \ln g(r, \bar{r}) + \beta u(|r - \bar{r}|) - [h(r, \bar{r}) - c(r, \bar{r})] + \lambda_{\bar{r}\bar{R}}(R) \tag{25}$$

A similar equation can be written for a PG field in the cell at R. These two equations combine to give

$$0 = \ln g(r, \bar{r}) + \beta u(|r - \bar{r}|) - [h(r, \bar{r}) - c(r, \bar{r})] + \Lambda_{R\bar{R}}(\bar{r}) + \Lambda_{\bar{R}R}(r) \quad (26)$$

where $\Lambda_{R\bar{R}}(\bar{r}) = \lambda_{\bar{r}\bar{R}}(R)/2$. Equation (26) is the constrained version of the HNC closure. As before, rearrangement and linearization produce the PY closure (constrained):

$$c(r, \bar{r}) = g(r, \bar{r})\{1 - \exp[\beta u(|r - \bar{r}|) + \Lambda_{R\bar{R}}(\bar{r}) + \Lambda_{\bar{R}R}(r)]\} \quad (27)$$

Note that the multipliers Λ are related to each other by symmetry. Since $g(r, \bar{r})$ approaches unity at large separations, where the constraints are satisfied, the Λ's approach zero as $|R - \bar{R}|$ becomes large.

In summary, the preliminary suggestion proposed in this section is that the OZ equation be solved with the constraint equations, (23) and (26), to obtain $g(r, \bar{r})$, $c(r, \bar{r})$, and $\Lambda_{R,\bar{R}}(\bar{r})$, rather than the liquid-state method of solving the OZ equation with Eq. (13) for $g(r, \bar{r})$ and $c(r, \bar{r})$. In the next section we see the results of a simple parameterization of the multipliers Λ and the effect of this on the pair correlation function.

5. RESULTS FOR THE CONSTRAINED PY CLOSURE

We discuss first the general nature of the constraints $\Lambda_{R\bar{R}}(\bar{r})$. In Fig. 4 we display a cell with its six nearest neighbors. For a two-point function

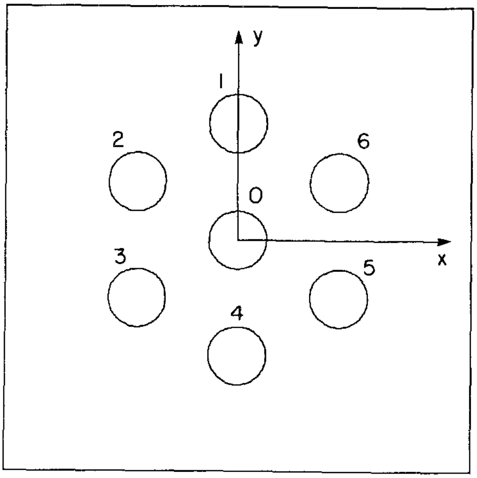

Fig. 4. The unit cells of the problem studied in this paper. Circles indicate the approximate range of the density peaks. The numbering and coordinate axes are used in our discussion.

which stretches from cell 0 to cell 1, the A's will play a role analogous to an external field interacting with the particles in cell 0 and cell 1. These "potentials" are not necessarily symmetric about the center of the cell. Now consider a second set of A's between cell 0 and cell 2; the A's are the same as before, except that they are rotated in space by 60°.

For the case of Gaussian density given by $\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, and $A = 0.7$, the number of particles per unit cell A was calculated from Eq. (15) for each point in cell 0 by integrating over cell 1. This calculated value is denoted by A_c. We have found that for points in the half of cell 0 with negative y values, the calculated value A_c is approximately correct. However, for points with positive y, the calculated value decreases steadily. At $y = 0.25\sigma$, A_c is roughly 0.1. Since there is very little variation of A_c in the x direction, a choice of $A_{1,0}(r_0)$ of the form

$$\begin{aligned} A_{1,0}(r_0) &= 0, && \text{if } y_0 < 0 \\ A_{1,0}(r_0) &= -my_0, && \text{if } y_0 > 0 \end{aligned} \tag{28}$$

is a reasonable first approximation for the constraint field. The subscripts 0, 1 indicate that the two-point functions reach between cell 1 and cell 0, and r_0 is a point in cell 0 with y component y_0. It is possible to choose "external fields" which enforce the constraints. Figure 5 displays $A_{0,1}(r_1)$

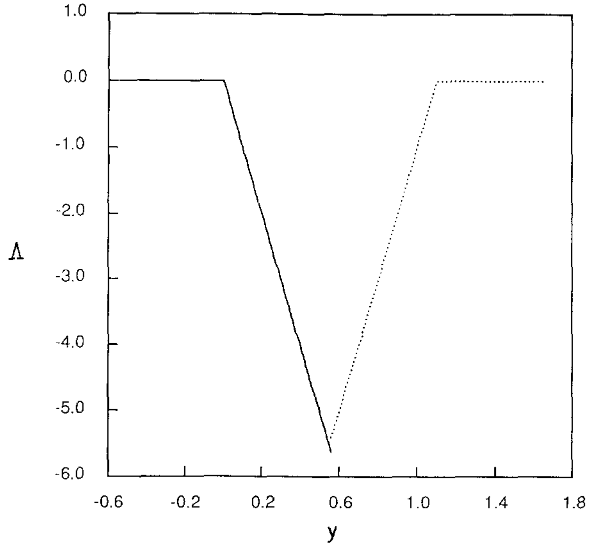

Fig. 5. The undetermined multipliers $A_{1,0}$ (solid line) and $A_{0,1}$ (dotted line) which enforce the constraints for $\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, and $A = 0.70$. They are plotted along the y axis of Fig. 4 (y in units of σ).

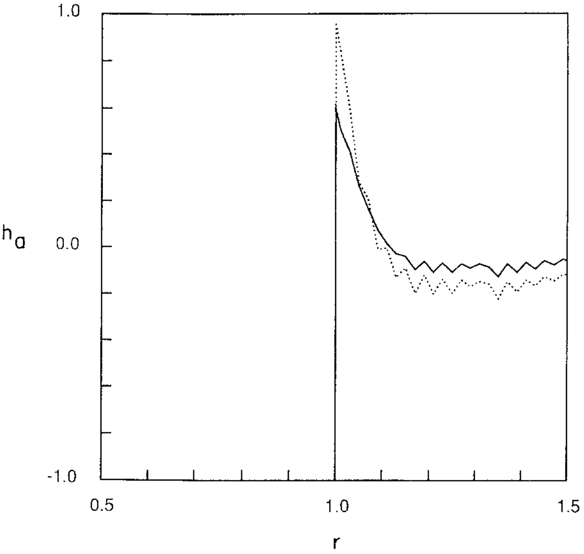

Fig. 6. The density-weighted pair correlation function h_a without (solid line) and with (dotted line) the constraints enforced, for the case $\varepsilon = 0.088\sigma$, $d = 1.10318\sigma$, and $A = 0.70$ (r in units of σ).

and $A_{1,0}(r_0)$ for this case. Figure 6 shows the density-weighted average $h_a(r)$ both before and after the constraints are imposed. Note the marked difference between the two. Clearly, Eq. (28) is very crude and the constraints have been enforced only in an approximate way, but this calculation suggests that generalizations of the PY closure are worth pursuing.

ACKNOWLEDGMENTS

This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society. ADJH also thanks Dr. Douglas Henderson for helpful discussions and Ford Motor Company and NSF for support through the Presidential Young Investigator Program.

REFERENCES

1. R. Lovett, C. Y., Mou, and F. P. Buff, *J. Chem. Phys.* **76**:570 (1976).
2. M. Werthiem, *J. Chem. Phys.* **65**:2377 (1976).
3. M. Plischke and D. Henderson, *J. Chem. Phys.* **84**:2846 (1986).

4. M. Plischke and D. Henderson, *J. Phys. Chem.* **88**:6544 (1984).
5. D. Henderson and M. Plischke, *Proc. R. Soc. Lond. A* **400**:163 (1985).
6. M. Plischke, D. Henderson, and S. R. Sharma, in *Physics of Disordered Materials*, D. Adler, H. Fritsche, and S. R. Ovshinsky, eds. (Plenum, New York, 1985), p. 97.
7. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
8. A. D. J. Haymet, *Annu. Rev. Phys. Chem.* **38**:89 (1987).
9. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964), p. II-171.
10. A. D. J. Haymet, *Chem. Phys. Lett.* **122**:324 (1985).
11. S. Sachdev and D. R. Nelson, *Phys. Rev.* **B33**:1480 (1985).
12. J. G. Kirkwood and E. Monroe, *J. Chem. Phys.* **8**:845 (1940); **9**:514 (1941).
13. J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**:116 (1963).
14. F. H. Stillinger and F. P. Buff, *J. Chem. Phys.* **37**:1 (1962).
15. A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, *J. Chem. Phys.* **64**:3732 (1976).
16. S. Sokolowski and W. A. Steele, *J. Chem. Phys.* **82**:2499, 3413 (1985).
17. R. Evans, *Adv. Phys.* **28**:143 (1979); see also D. Mermin, *Phys. Rev.* **A137**:1441 (1965).
18. T. V. Ramakrishnan and M. Yussouff, *Phys. Rev.* **B19**:2775 (1979).
19. A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.* **74**:2559 (1981).
20. D. W. Oxtoby and A. D. J. Haymet, *J. Chem. Phys.* **76**:6262 (1982).
21. A. D. J. Haymet, *J. Chem. Phys.* **78**:4641 (1983).
22. S. Rick and A. D. J. Haymet, *J. Chem. Phys.* **90**:1188 (1989).
23. S. J. Smithline, S. Rick, and A. D. J. Haymet, *J. Chem. Phys.* **88**:2004 (1988).
24. B. B. Laird, J. D. McCoy, and A. D. J. Haymet, *J. Chem. Phys.* **88**:3900 (1988); **87**:5449 (1987).
25. R. McRae and A. D. J. Haymet, *J. Chem. Phys.* **88**:1114 (1988).
26. Y. Singh, J. P. Stoessel, and P. G. Wolynes, *Phys. Rev. Lett.* **54**:1059 (1985).
27. M. Rovere and M. P. Tosi, *J. Phys.* **C18**:3445 (1985).
28. J. L. Barrat, M. Baus, and J. P. Hansen, *Phys. Rev. Lett.* **56**:10 (1986).
29. M. Baus and J. L. Colot, *Mol. Phys.* **55**:653 (1985); see also *Mol. Phys.* **57**:809 (1986).
30. G. Jones and U. Mohanty, *Mol. Phys.* **54**:1241 (1985).
31. P. Tarazona, *Phys. Rev.* **A31**:2673 (1985); **A32**:3148 (1985).
32. F. Igloi and J. Hafner, *J. Phys.* **C19**:5799 (1986).
33. W. Curtin and W. Ashcroft, *Phys. Rev.* **A32**:2909 (1985).
34. P. Radloff, B. Bagchi, C. Cerlan, and S. A. Rice, *J. Chem. Phys.* **81**:1406 (1984).
35. D. Chandler, J. D. McCoy, and S. J. Singer, *J. Chem. Phys.* **85**:5971, 5977 (1986).