PHYSICAL REVIEW E VOLUME 50, NUMBER 3 SEPTEMBER 1994

Temperature dependence of pair correlations and correlation entropy in a fluid

Carlos R. Sanchez-Castro, John B. Aidun, Galen K. Straub, John M. Wills, and Duane C. Wallace
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 21 March 1994)

For a system of atoms interacting through a pair potential, the entropy is evaluated by molecular dynamics at temperatures from the liquid to the gas. The pair potential represents aluminum in the liquid regime and the calculated entropy is in close agreement with experiment. The temperature dependence of the entropy is understood in terms of structural changes in the pair correlation function. Of the two approximate entropy expansions evaluated in low orders, the Nettleton-Raveché-Green expansion is more accurate at high temperatures, while the multiparticle irreducible correlation expansion is more accurate for the liquid.

PACS number(s): 05.20.−y, 05.70.Ce, 65.50.+m

I. INTRODUCTION

Our goal is to use molecular dynamics (MD) calculations to make a comparison of approximate entropy formulas with the exact entropy, for a single system at temperatures from the liquid to the gas. In classical statistics, the difficult part of the entropy is the correlation entropy, arising from the configuration integral in the partition function. In the following section, mention is made of the virial expansion for a gas, and then two expansions are described which have a chance of converging well for a liquid, namely, the Nettleton-Green-Raveché (NGR) expansion, and the multiparticle irreducible correlation (MIC) expansion. MD evaluations of the exact entropy, and also of each of these expansions correct to second order, are presented in Sec. III. It is concluded in Sec. IV that the MIC expansion is more accurate for a liquid, while the NGR expansion is more accurate at temperatures approaching the gas regime.

We work with entropy in units of k_B per atom, where k_B is the Boltzmann's constant. For an elemental liquid at around the melting temperature T_m, the total entropy is ≈ 10, the correlation entropy is ≈ -2.6, the entropy of melting is ≈ 1.0, and an excellent theory of entropy should be accurate to ± 0.1, which is also the level of accuracy attained by quasiharmonic lattice dynamics theory for the crystalline state.

II. APPROXIMATE ENTROPY FORMULAS

Let us consider a system of N like atoms in a volume V, with particle density $\rho = N/V$. The entropy S in the canonical ensemble is [1]

$$S = S_1 + S_c \ , \tag{1}$$

where the one-particle term is

$$S_1 = -\rho^{-1} \int f^{(1)}(\mathbf{p}) \ln[h^3 f^{(1)}(\mathbf{p})] d\mathbf{p} \ . \tag{2}$$

The integral can be done, since $f^{(1)}(\mathbf{p})$ is the normalized Boltzmann distribution, yielding

$$S_1 = \tfrac{3}{2} - \ln(\rho\Lambda^3) \ , \tag{3}$$

where $\Lambda = h(\beta/(2\pi M))^{1/2}$ is the de Broglie wavelength, M is the particle mass, and $\beta = (k_B T)^{-1}$. The correlation entropy S_c arises from the configuration integral in the partition function, and is expressed [1] as

$$S_c = -N^{-1}(\rho^N/N!) \int \cdots \int g^{(N)} \ln g^{(N)} d\mathbf{r}_1 \cdots d\mathbf{r}_N \ , \tag{4}$$

where $g^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the N-particle correlation function, with $\mathbf{r}_i$ being the particle positions. These equations are valid at all temperatures and densities where classical statistics apply. However, the N-particle integral in S_c is generally intractable, so it is useful to develop approximations for this integral.

We first examine the gas regime. The correlation function $g^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ depends on the total system potential $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, and in the physically realistic case, where Coulomb forces are screened, and where there are no infinite hard cores, the total system potential is spatially integrable. This means the gas regime is reached both at low densities ($\rho \rightarrow 0$), and at high temperatures ($\beta \rightarrow 0$) [2]. Under either of these conditions, the virial expansion can be made, yielding

$$S_c = 1 + S_v^{(2)} + \cdots \ , \tag{5}$$

where $S_v^{(2)} + \cdots$ represents the virial series, a power series in ρ [3]. The value 1 expresses that each particle moves freely throughout the entire system volume; the series $S_v^{(2)} + \cdots$ expresses interference of this free motion, from the atomic interactions, and is negative, hence reduces S_c from the ideal gas value of 1. The virial expansion has a radius of convergence [4], which presumably does not extend to the liquid regime.

Before we can approximate S_c for a liquid, we need to recognize the physically spurious long range correlation present in constant-N ensembles. First, in any ensemble, there is presumed to exist a correlation length l_c [5], normally a few nearest-neighbor distances, beyond which the two particle correlation vanishes, as indicated by the condition $g^{(2)}(r) = \text{const}$ for $r > l_c$. In the grand canonical ensemble this constant is 1, and the normalization is

$$\rho \int [g^{(2)}(r) - 1] d\mathbf{r} = -1 + \alpha \ , \tag{6}$$

where $\alpha = k_B T\rho\kappa$, and $\kappa \equiv -(\partial \ln V/\partial P)_{T,N}$ is the isothermal compressibility. The variable α is a measure of the density fluctuations, and is positive; $\alpha \ll 1$ for a liquid, and $\alpha \approx 1$ for a gas. In the canonical ensemble, $g^{(2)}(r)$ has a nonphysical long range correlation because, given a particle at any position, the number of remaining particles is exactly $N-1$. Thus, $g^{(2)}(r) = 1-\alpha/N$ for $r > l_c$ [6], and the normalization is

$$\rho \int [g^{(2)}(r)-1]d\mathbf{r} = -1 \ . \tag{7}$$

To obtain the same normalization in any ensemble, we limit the integration to $r \le l_c$, denoted by $\int_c d\mathbf{r}$, and find

$$\rho \int_c [g^{(2)}(r)-1]d\mathbf{r} = -1+\alpha+O(N^{-1}) \ . \tag{8}$$

This result is valid for all ensembles, since $g^{(2)}(r)$ is the same to order N^{-1} in all ensembles [7]. Analogous properties hold for higher correlation functions $g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$.

Turning to the correlation entropy for a liquid, we note the motion of particles in a liquid represents an opposite extreme from a gas: in a liquid there is essentially no free particle motion, but rather, each particle moves within a cage formed by its neighbors. Hence in a liquid, the important correlation is contained in the $g^{(n)}$ for small n, specifically for $n = 2,3,\ldots$. This concept led Green [8] to the multiparticle correlation expansion of $\ln g^{(N)}$ in the canonical ensemble, the first term of which is $(\frac{1}{2})\Sigma_{ij}\ln g_{ij}^{(2)}$. However, the spatial integral of Green's expansion contains the nonphysical long range correlations resulting from the constant-N condition. In the past, we eliminated this problem by using grand canonical correlation functions [1,9]. Here we will limit the integrations to within the correlation length, giving results valid in all ensembles:

$$S_c = S_2 + S_3 + \cdots \ , \tag{9}$$

where

$$S_2 = -\tfrac{1}{2}\rho \int_c g^{(2)}(r)\ln g^{(2)}(r)d\mathbf{r} \ . \tag{10}$$

Equation (9) is denoted the multiparticle irreducible correlation (MIC) expansion, since each term S_n depends on irreducible n-particle correlations, that is, correlations which are not contained in lower-order correlation functions [1,9]. Hence the relevant expansion parameter is the number n of correlated particles. This expansion is expected to converge rapidly for the highly correlated liquid state, and by now there is strong support of this convergence, as summarized in Sec. IV.

In Green's original expansion of the complete entropy [8], the one-particle term is undefined [9], and the multiparticle terms contain the physically spurious long range correlation of the canonical ensemble. To eliminate this long range correlation, Nettleton and Green [10] constructed a grand canonical expansion in powers of the density, and in the process they fixed the one particle term at the ideal gas value S_1+1. This expansion was also discussed by Yvon [11]. An alternate derivation was given by Raveché [12], and was evaluated for liquid models by Mountain and Raveché [13]. Let us write the Nettleton-Green-Raveché (NGR) expansion as

$$S_{\text{NGR}} = S_{\text{NGR}}^{(1)} + S_{\text{NGR}}^{(2)} + \cdots \ . \tag{11}$$

Each term $S_{\text{NGR}}^{(n)}$, for $n \ge 2$, contains the irreducible correlation term S_n, plus a cumulant expression having correlation functions of every order up to n. Specifically,

$$S_{\text{NGR}}^{(1)} = S_1 + 1 \ , \tag{12a}$$

$$S_{\text{NGR}}^{(2)} = S_2 + \tfrac{1}{2}\rho \int [g^{(2)}(r)-1]d\mathbf{r} \ , \tag{12b}$$

and so on. Since the relevant expansion parameter is the density, the NGR expansion has the correct limit in the gas regime.

The NGR and the MIC expansions are merely rearrangements of one another. Hence, while they differ term by term, each has the same formal sum when carried to all orders. In the liquid regime, aside from very small terms in α, the NGR expansion differs by the amount n^{-1}, in order n, from the MIC expansion [1]. The difference n^{-1} is crucial in practical applications, where S is needed to an accuracy of around ±0.1.

For completeness, we should mention some related entropy studies. Fisher [14] derived an entropy expansion in which the one-particle term is S_1+1, while the two-particle term is S_2. Faber [15] tested this expansion for Al and Hg, and concluded correctly that it is inaccurate. Baranyai and Evans [16,17] express the opinion that the MIC expansion cannot be correct because it differs term by term from the NGR expansion.

III. MOLECULAR DYNAMIC CALCULATIONS

The Hamiltonian is taken to be

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2M} + \frac{1}{2}\sum_{i,j=1}^{N} \phi_{ij} \ , \tag{13}$$

where $\mathbf{p}_i$ is the momentum of atom i, and $\phi_{ij} = \phi(|\mathbf{r}_i - \mathbf{r}_j|, V)$ is a two-body central potential. The effective interaction between ions $\phi(r,V)$ was calculated [18] using pseudopotential theory and consists of the sum of a direct Coulomb repulsion between the ionic cores and a volume dependent induced interaction mediated by the electrons. We study the classical statistical mechanics of this system at the fixed density $\rho_1 = 0.063\,276$ Å^{-3}, and at temperatures from melting to the virial regime. Our MD calculations are done with the Verlet algorithm, for systems containing $N = 864-4032$ atoms, with periodic boundary conditions.

This study was undertaken as part of a program to calculate *ab initio* thermodynamic properties of metallic aluminum [18]. Hence ρ_1 is close to the density 0.061 025 Å^{-3} of aluminum at zero temperature and pressure, and the potential $\phi(r,V)$ was constructed to model real aluminum at density ρ_1, and at temperatures where the valence electrons are approximately in their ground state, i.e., where $k_B T$ is small compared with the Fermi energy ϵ_F. At higher temperatures the electrons become strongly excited, and the Hamiltonian no longer represents aluminum. In other words, the Hamiltonian given by Eq. (13) describes the low lying states of Al, and its thermodynamical properties will correspond with those of real aluminum [19] at temperatures $T < \epsilon_F / k_B$, where only those low lying states determine the statistical mechanics of both systems. Indeed, the calculations presented here were utilized for an accurate *ab initio* determination of the entropy of liquid aluminum [18]. Note for aluminum at ρ_1, $\epsilon_F = 0.62$ Ry, $T_m \approx 1860$ K$=0.0118$ Ry, and our results represent real aluminum for T at least to $10T_m$.

To determine the entropy in the fluid phase of the system described by the Hamiltonian in Eq. (13), it is necessary to calculate the internal energy as a function of the temperature, up to the very high temperatures where the virial expansion can be used to evaluate the entropy constant. This procedure will now be described.

The mean potential energy per atom, evaluated by MD and denoted by U_ϕ, is shown in Fig. 1, and displays the two important characteristics found in our study of metallic sodium [2]. (a) At temperatures just above T_m, the slope of U_ϕ vs $k_B T$ is $\frac{3}{2}$, within 5%. Since the mean kinetic energy per atom is $(\frac{3}{2}) k_B T$, then the liquid has specific heat at constant volume $C_V \approx 3k_B$ at T_m, and C_V decreases slowly as T increases. Hence the atomic motional energy of the liquid corresponds to $3N$ harmonic oscillators. (b) Since $\phi(r,V)$ is integrable, then U_ϕ saturates at high temperatures to the known limit [2] $U_\phi = \frac{1}{2}\langle \phi \rangle$, and C_V approaches $\frac{3}{2} k_B$. Here,

$$\langle \phi \rangle = 4\pi\rho \int_0^\infty \phi(r,V) r^2 dr \qquad (14)$$

and $\frac{1}{2}\langle \phi \rangle = 1.73 \pm 0.02$ Ry for our present potential. Hence at very high temperatures, the kinetic energy dominates the potential, the atoms move nearly as free particles, and the system is a gas.

Similarly, as shown in Fig. 2, the contribution to the pressure from the internal virial, P_ϕ, which for a metallic system is given by [20]

$$P_\phi = -\rho^2 \int_0^\infty 2\pi r^2 g^{(2)}(r) \left[\frac{r}{3} \frac{\partial \phi}{\partial r} + V \frac{\partial \phi}{\partial V} \right] dr , \qquad (15)$$

saturates at very high temperatures and the law $P = \rho k_B T$ is obeyed.

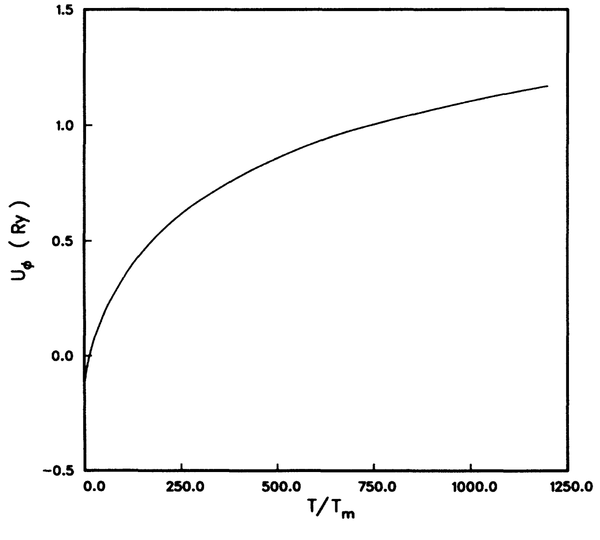

FIG. 1. Mean potential energy per atom, from MD calculations, from $T/T_m = 1.1372$ up to 1199.6. On the scale shown, $T/T_m = 1.1372$ is indistinguishable from zero.

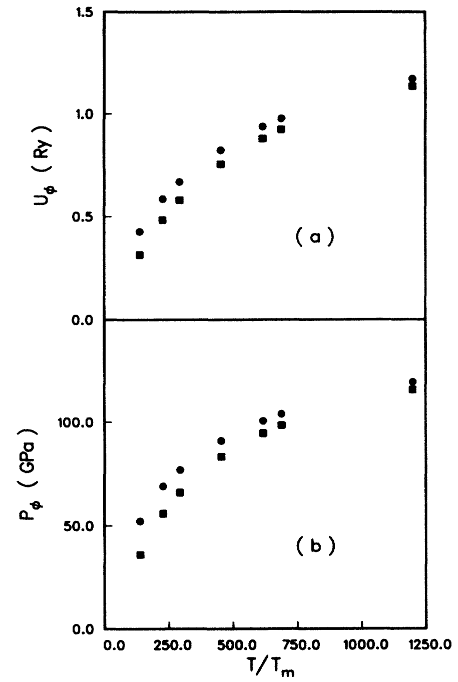

FIG. 2. (a) The mean potential energy per atom as a function of T/T_m from MD simulations (circles) and the virial expansion (squares). (b) The internal virial contribution to the pressure as a function of T/T_m from MD simulations (circles) and the virial expansion (squares).

The virial expansion for a metallic system at constancy density yields [2]

$$\beta U_\phi = -\rho \left. \frac{\partial B_2}{\partial \ln T} \right|_{V,N} + \cdots , \qquad (16)$$

$$\beta P_\phi = \left[B_2 - \left. \frac{\partial B_2}{\partial \ln V} \right|_{T,N} \right] \rho^2 + \cdots , \qquad (17)$$

where

$$B_2 = 2\pi \int_0^\infty (1 - e^{-\beta\phi(r,V)}) r^2 dr , \qquad (18)$$

and where $+\cdots$ represents terms in higher virial coefficients. The approach of our MD system to the virial limit is shown in Fig. 2. At the highest temperature considered, $k_B T_{\max} = 14.1308$ Ry, the internal energy per particle $U = (\frac{3}{2}) k_B T + U_\phi$, and the pressure $P = k_B T \rho + P_\phi$ calculated from the virial expansion agree with those of the MD simulation to 0.16% and 0.19%, respectively. The discrepancy is due to the neglect of higher-order terms in the virial expansion. The entropy, calculated from the virial expansion, Eq. (5),

$$S_v^{(2)} = -\rho \left[B_2 + \left. \frac{\partial B_2}{\partial \ln T} \right|_{V,N} \right] , \tag{19}$$

and an estimate of B_3, gives $S = 23.534 \pm .002$ at $T_{\max}$. The entropy at lower temperatures [21] is then calculated by using the thermodynamic identity

$$S(T) - S(T_{\max}) = \frac{U(T)}{T} - \frac{U(T_{\max})}{T_{\max}} + \int_{T_{\max}}^{T} dT' \frac{U(T')}{T'^2} , \tag{20}$$

at fixed volume and number of particles. Here the internal energy per particle, U, is determined from MD simulations.

The pair correlation function $g(r) \equiv g^{(2)}(r)$ was also evaluated from the MD calculations, and a series of $g(r)$ at various temperatures is shown in Fig. 3. For T just above T_m, the height of the nearest-neighbor peak is 2.8, and six neighbor shells are clearly visible. As T increases, the height of the first peak drops, the shell structure gradually disappears, and the nearest-neighbor shoulder moves to smaller distances. For $T \gtrsim 100 T_m$, $g(r)$ approaches its virial limit of $e^{-\beta\phi(r,V)}$.

When we analyze our $g(r)$ data, the limit at large r is 1 within error estimates. However, when we numerically integrate $g(r) - 1$, the integral shows a drift as a function of its upper limit R, at large R, consistent with the canonical value $1 - \alpha/N$ for $g(r)$ at large r. This property yields a value of the correlation length l_c, which is a function of temperature. Results for α, obtained by evaluating the integral in Eq. (8), are graphed in Fig. 4, and show the expected behavior: $\alpha \ll 1$ at low temperatures in the liquid regime, and α increases toward 1 as temperature increases toward the gas regime.

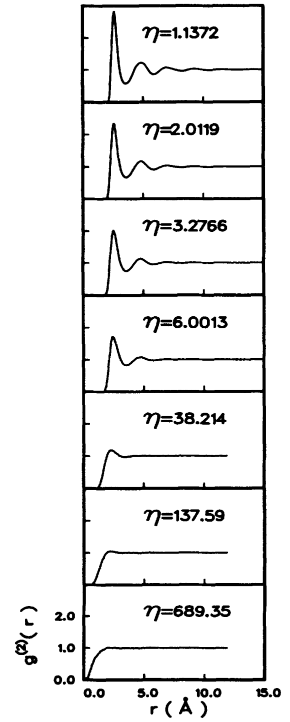

FIG. 3. Pair correlation functions, showing transition from liquid to gas behavior, as $\eta = T/T_m$ increases.

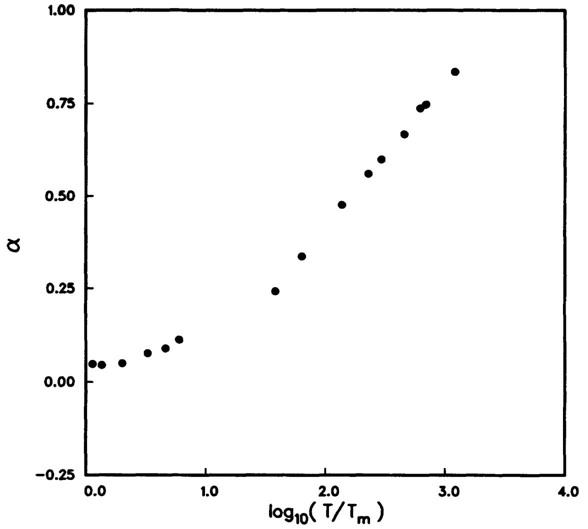

FIG. 4. Density fluctuation parameter α vs $\log(T/T_m)$ (the log base is 10).

The exact correlation entropy $S_c = S - S_1$ is shown in Fig. 5, and is compared with the two entropy expansions, in second order:

$$S_c = 1 + S_{\mathrm{NGR}}^{(2)}, \quad \mathrm{NGR}, \tag{21a}$$

$$S_c = S_2, \quad \mathrm{MIC}, \tag{21b}$$

where $S_{\mathrm{NGR}}^{(2)}$ is given by Eq. (12) and S_2 is given by Eq. (10). Figure 5 exhibits the behavior previously predicted

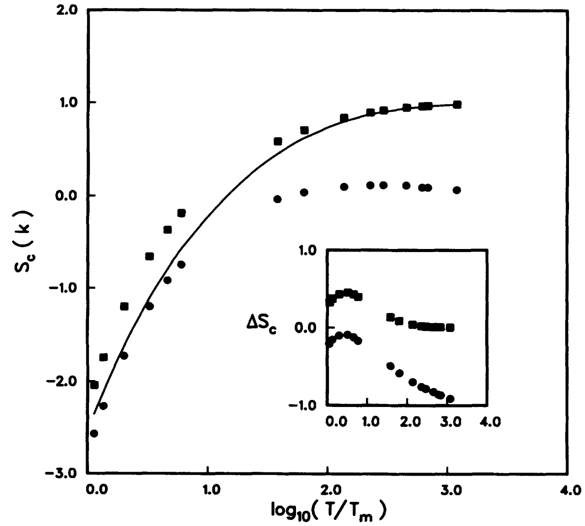

FIG. 5. The exact correlation entropy (solid line), the NGR (squares) and the MIC expansions (circles) to second order, as a function of T/T_m. The inset shows the deviations of the two expansions from the exact correlation entropy.

[1,9]: in second order, the MIC expansion is more accurate for the liquid, while the NGR expansion is more accurate for the gas.

IV. DISCUSSION

In the graph of α vs T, Fig. 4, α will continue to increase, and approach 1, as T increases above $10^3 T_m$. The temperature dependence of α shows three qualitative regimes for the system studied here: the liquid for $T \lesssim 10T_m$ ($\alpha \ll 1$); the regime intermediate from liquid to gas; and the gas for $T \gtrsim 10^3 T_m$ ($\alpha \approx 1$). This is consistent with the fact that we reach the virial limit, i.e., the virial expansion becomes highly accurate, for $T \gtrsim 10^3 T_m$. It is seen from Fig. 3 that the pair correlation function exhibits shell structure throughout the liquid regime, while in the intermediate regime there is only a remnant of shell structure, and the main characteristic of pair correlation is the excluded volume at close range.

The two entropy expansions considered here, the NGR and the MIC expansions, are both formally correct. However, they differ term by term, and the practical question is, how well do they represent the entropy in low order? In the virial regime, the NGR expansion is accurate in low order, since it approaches the virial expansion term by term, while the MIC expansion is inaccurate in low order, since the low-order terms completely miss the ideal gas correlation entropy of 1 [1]. At lower temperatures, when the expansions are evaluated to second order, each has its region of applicability, as shown in Fig. 5: The MIC expansion is more accurate for the liquid, while the NGR expansion is more accurate for the upper part of the intermediate regime. Similar behavior is apparent in the results given previously for hard spheres [1].

An extensive examination of the entropy of liquid metals has been carried out [22], in which S_2 was calculated from experimental data for $g(r)$, and the entropy of thermal excitation of the valence electrons was accounted for. The conclusions are (a) the terms $S_1 + S_2$ alone generally represent the ion motional entropy to within the combined errors of the analysis, which in many cases is to an accuracy of ± 0.1, and (b) exception of this behavior for a few metals and semimetals is attributed to higher-order correlation entropy, which turns out to be negative in all cases, and which is associated with the presence of many body forces. Further, except for those "anomalous" elements which undergo a change in electronic structure upon melting [23], the zero pressure experimental results for S_2 vs (T/T_m) display approximately universal behavior for all elemental liquids, in agreement with the behavior shown by S_2 in Fig. 5.

[1] D. C. Wallace, Phys. Rev. A **39**, 4843 (1989).

[2] D. C. Wallace, B. L. Holian, J. D. Johnson, and G. K. Straub, Phys. Rev. A **26**, 2882 (1982).

[3] See, for example, D. A. McQuarrie, *Statistical Mechanics* (Harper, New York, 1976), Chap. 12.

[4] D. Ruelle, *Statistical Mechanics* (Benjamin, New York, 1969), Sec. 4.3.

[5] J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1675 (1961).

[6] E. Feenberg, *Theory of Quantum Liquids* (Academic, New York, 1969), Chap. 1.

[7] See, for example, Eq. (19) of Ref. [1].

[8] H. S. Green, *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952), Chap. III, Sec. 5.

[9] D. C. Wallace, J. Chem. Phys. **87**, 2282 (1987).

[10] R. E. Nettleton and M. S. Green, J. Chem. Phys. **29**, 1365 (1958).

[11] J. Yvon, *Correlations and Entropy in Classical Statistical Mechanics* (Pergamon, Oxford, 1969), Sec. 3.8.

[12] H. J. Raveché, J. Chem. Phys. **55**, 2242 (1971).

[13] R. D. Mountain and H. J. Raveché, J. Chem. Phys. **55**, 2250 (1971).

[14] I. Z. Fisher, *Statistical Theory of Liquids* (University of Chicago Press, Chicago, 1964), Eqs. (2.90) and (2.91).

[15] T. E. Faber, *Theory of Liquid Metals* (Cambridge University Press, Cambridge, 1972). Sec. 2.9.

[16] A. Baranyai and D. J. Evans, Phys. Rev. A **40**, 3817 (1989).

[17] A. Baranyai and D. J. Evans, Phys. Rev. A **42**, 849 (1990).

[18] G. K. Straub, J. B. Aidun, J. M. Wills, C. R. Sanchez-Castro, and D. C. Wallace, Phys. Rev. B **50**, 5055 (1994).

[19] More precisely, to represent real aluminum, a static structural potential and an electronic term have to be added to Eq. (13) [18].

[20] D. C. Wallace and G. K. Straub, Phys. Rev. A **27**, 2201 (1983).

[21] B. L. Holian, G. K. Straub, R. E. Swanson, and D. C. Wallace, Phys. Rev. B **27**, 2873 (1983).

[22] D. C. Wallace, Proc. R. Soc. London Ser. A **433**, 615 (1991).

[23] D. C. Wallace, Proc. R. Soc. London Ser. A **433**, 631 (1991).