

EQUILIBRIUM STRUCTURE OF SIMPLE LIQUIDS*

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It is shown that the repulsive (not merely the positive) portion of the Lennard-Jones potential quantitatively dominates the equilibrium structure of the Lennard-Jones liquid. A simple and accurate approximation for the radial distribution function at high densities is presented.

It is often remarked that the repulsive forces in a simple liquid play an important role in forming the equilibrium structure of such a fluid.¹⁻³ By studying the spectrum (Fourier transform) of the two-particle correlation function,

$$\hat{h}(k) = \rho \int [g(r) - 1] e^{-i\vec{k} \cdot \vec{r}} d\vec{r}, \quad (1)$$

where $g(r)$ is the usual radial distribution function and ρ is the average number density, we are able to formulate this idea in a precise and useful way.

In order that a convenient basis for comparison be available, the Lennard-Jones fluid is considered: a classical N -particle system in which the total potential energy is a sum of the Lennard-Jones pair potentials, $w(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. Our attention is focused on $\hat{h}(k)$ for the Lennard-Jones liquid. In particular, for liquid densities ($\rho\sigma^3 \gtrsim 0.4$) we hypothesize and then verify the following statements: (1) At intermediate and large wave vectors ($k\sigma \gtrsim \pi$) the quantitative behavior of $\hat{h}(k)$ is dominated by the repulsive forces (the attractive forces are primarily manifested in the small-wave-vector portion of the spectrum). (2) For high densities ($\rho\sigma^3 \gtrsim 0.65$) the behavior of $\hat{h}(k)$ even at small wave vectors ($k\sigma \lesssim \pi$) is at least qualitatively determined by the repulsive forces. Physically, the first statement is understood once it is recalled that $\hat{h}(k) + 1$ represents the linear response of the fluid structure to a disturbance of wavelength $2\pi/k$.⁴ While a short-wavelength disturbance will probe both the repulsive and attractive forces in a fluid, it is reasonable that the presence of the harsh repulsions, rather than the slowly varying longer ranged attractions, will dominate the response of the fluid to such a disturbance. The second statement is equivalent to asserting that the correlations in a simple liquid are almost entirely due to excluded-volume effects when the density is high. While this latter part of our hypothesis has been stated qualitatively by many authors,¹⁻³ its quantitative validity has not been appreciated.

To see how the repulsive portion of the pair potential affects the liquid structure, it is con-

venient to consider a reference system in which the pair potential, $u_0(r)$, contains all the repulsive forces implied by the Lennard-Jones potential, $w(r)$, and no attractive forces. With the additional condition that the reference system has a well-defined thermodynamic limit, $u_0(r)$ is defined uniquely,

$$\begin{aligned} u_0(r) &= w(r) + \epsilon, \quad r < 2^{1/6}\sigma, \\ &= 0, \quad r \geq 2^{1/6}\sigma. \end{aligned} \quad (2)$$

It should be noted that the repulsive part of $w(r)$ is the portion with negative slope and not the portion which is merely positive. In terms of the radial distribution function for the reference system, $g_0(r)$, and its spectrum, $\hat{h}_0(k)$, the hypotheses stated above can be expressed as follows: At all liquid densities, the approximation $\hat{h}_0(k) \approx \hat{h}(k)$ is very accurate for $k\sigma \gtrsim \pi$; at high densities ($\rho\sigma^3 \gtrsim 0.65$), $g(r)$ closely resembles $g_0(r)$. Thus, the task of verifying our hypotheses is reduced to determining $g_0(r)$ and $\hat{h}_0(k)$. Rather than perform expensive machine calculations to obtain this information, we have invented an approximation method to describe the reference system. Tests have been performed⁵ which indicate that our treatment is certainly accurate enough for the purposes of this work. To discuss the method, we introduce the function $y_0(r)$ which is defined by the equation

$$g_0(r) = y_0(r) \exp[-\beta u_0(r)], \quad (3)$$

where $\beta = (k_B T)^{-1}$. Physically, $y_0(r)$ gives the correlations that exist in the reference system beyond the range of the reference interaction $u_0(r)$. Since this interaction is harshly repulsive, it seems probable that $y_0(r)$ can be approximated by the similar function appropriate to a hard-sphere system of diameter d , $y_d(r)$. For this reason, we consider the following approximation:

$$g_0(r) \approx y_d(r) \exp[-\beta u_0(r)] \quad (4)$$

or

$$\hat{h}_0(k) \simeq \hat{h}_d(k) + \rho \int d\vec{r} y_d(r) (e^{-\beta u_0} - e^{-\beta u_d}) e^{-i\vec{k}\cdot\vec{r}}, \quad (4')$$

where $\hat{h}_d(k)$ denotes the spectrum for the hard-sphere system of diameter d , and u_d denotes a hard-core repulsion of diameter d . By recalling the role of $\hat{h}_0(k)$ as a linear response function, it is seen that Eq. (4) is equivalent to assuming that for intermediate- and long-wavelength disturbances, the response of the reference system is accurately given by the response of a hard-sphere system. Thus, by equating the long-wavelength (small- k) responses of the reference and hard-sphere systems, we have a physically reasonable density- and temperature-dependent criterion for determining d :

$$\int d\vec{r} (y_d e^{-\beta u_0} - 1) = \int d\vec{r} (y_d e^{-\beta u_d} - 1). \quad (5)$$

Finally, for lack of better analytic or extensively tabulated hard-sphere functions, we use the analytic solution of the Percus-Yevick equation to give us $\hat{h}_d(k)$ and $y_d(r)$ ($0 < r < 2d$).⁶ Though it is fairly accurate, it represents our major source of error in the computations reported below.

When Eq. (5) is solved for $d(\beta, \rho)$ and plotted along several isochores, graphs are obtained⁵ that are very similar to those given by Verlet (Fig. 17, Ref. 1) for the effective hard-sphere diameter needed to empirically "fit" a hard-sphere spectrum $\hat{h}_d(k)$ to the Lennard-Jones spectrum $\hat{h}_0(k)$ at intermediate wave vectors. Thus, we believe Verlet was observing the behavior we have hypothesized: For $k\sigma \gtrsim \pi$, the spectrum is dominated by the repulsive (reference) forces. In Fig. 1, we plot $\hat{h}_0(k)$ (as obtained from our treatment of the reference system) at two thermodynamic states (labeled I and II) and compare with Verlet's molecular-dynamics results.¹ For state I, the density is sufficiently low to illustrate the dramatic discrepancy and then similarity between $\hat{h}_0(k)$ and the true Lennard-Jones spectrum as we pass from small to large wave vectors. Incidentally, for state I the value of d obtained from Eq. (5) is 1.005σ ; Verlet reports a hard-sphere-model d of 1.0σ . From the curve for state II, we see that at high densities the excluded-volume effects dominate the correlations to such an extent that $\hat{h}_0(k)$ is also in good agreement with the Lennard-Jones spectrum for small wave vectors. The value of d for this thermodynamic state is 1.025σ ; Verlet's hard-sphere-model d is 1.026σ .

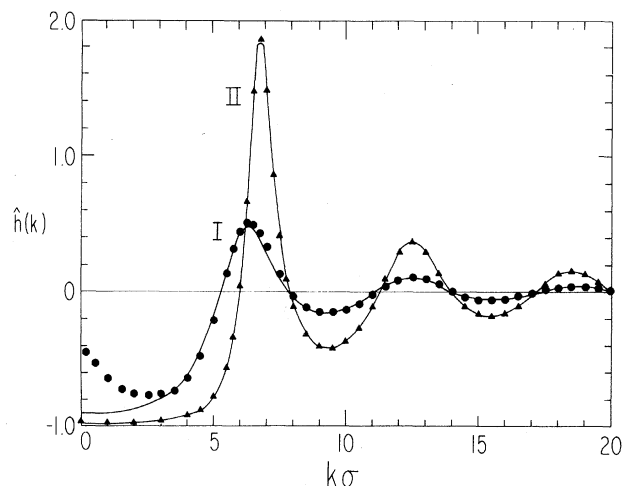


FIG. 1. Plots of $\hat{h}(k)$ for two thermodynamic states: State I is $\rho\sigma^3 = 0.5426$, $(\beta\epsilon)^{-1} = 1.326$; state II is $\rho\sigma^3 = 0.844$, $(\beta\epsilon)^{-1} = 0.723$. The lines represent Eq. (4'); the circles and triangles denote the molecular-dynamics results (Ref. 1) for states I and II, respectively.

The agreement between $\hat{h}_0(k)$ and $\hat{h}(k)$ that is observed at high densities implies that $g_0(r)$ should closely resemble $g(r)$ (except for very large r) at high densities. In Fig. 2 a plot of $g_0(r)$ as described in Eq. (4) is compared with the "exact" Lennard-Jones¹ $g(r)$; the thermodynamic state is similar to state II in Fig. 1. The agreement between $g_0(r)$ and $g(r)$ is excellent. To emphasize how accurate it is, we have also plotted the $g(r)$ obtained by solving the Percus-Yevick equation for the Lennard-Jones fluid.^{6a,7} We mention that the Fourier inversion of $\hat{h}_0(k)$ at a moderate density (e.g., the thermodynamic state I considered in Fig. 1) agrees poorly with the Lennard-Jones $g(r)$ for all r .⁵ This behavior is a manifestation of the discrepancy between $\hat{h}_0(k)$ and $\hat{h}(k)$ for small k . It emphasizes the convenience of considering the spectral representation of the structure rather than $g(r)$ itself. While the attractive forces appreciably contribute to only a small part of the spectrum, $k\sigma \lesssim \pi$, the attractions and repulsions contribute (at low and moderate densities) to $g(r)$ for all $r \gtrsim \sigma$. Thus, it is difficult to say what type of interaction produces a certain effect in $g(r)$. Our results indicate that this difficulty is not encountered when the spectrum is considered.

Finally, as a further check on the accuracy of the approximation $g_0(r) \simeq g(r)$ at high densities, we replace $g(r)$ by $g_0(r)$ in the pressure (virial) equation,

$$\beta p / \rho = 1 + (\beta\rho/6) \int r [\partial w(r) / \partial r] g(r) d\vec{r}, \quad (6)$$

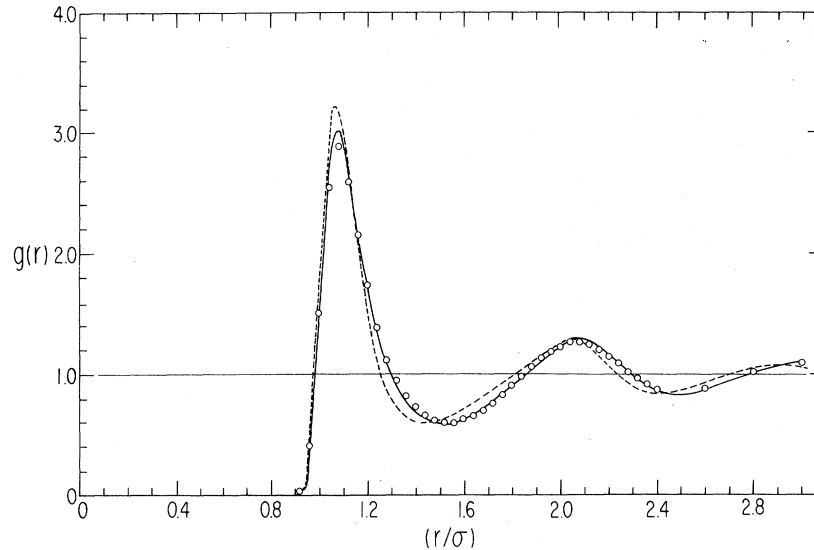


FIG. 2. Plots of $g(r)$ at a high density: $\rho\sigma^3=0.85$, $(\beta\epsilon)^{-1}=0.88$. The line represents the approximation $g_0(r) \approx g(r)$; the circles are molecular-dynamics results (Ref. 1); the dashed line represents the numerical solution of the Percus-Yevick equation for the Lennard-Jones potential (Ref. 7).

and in the energy equation for the excess internal energy,

$$\beta\Delta E/N = (\beta\rho/2) \int w(r)g(r)d\vec{r}. \quad (7)$$

Once again, the calculations were performed within the context of our approximate treatment of the reference system. A few of our results are presented in Table I and compared with those obtained from molecular dynamics⁸ and the numerical solution of the Percus-Yevick equation for the Lennard-Jones system.⁷ These results are representative of those found when a far more extensive comparison with molecular dynamics is made at several high densities ($\rho\sigma^3 \geq 0.65$).⁵

It is our opinion that we have demonstrated the validity of the hypotheses stated at the beginning

of this report. In so doing we have also discovered a very simple and accurate theory for the structure of dense liquids: namely the approximation $g(r) \approx g_0(r)$ combined with Eq. (4). In a future publication,⁵ our ideas will be documented more thoroughly. At that time we will also discuss, in detail, the relevance of our hypothesis to perturbation theories for liquids.²

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Table I. Approximate and molecular-dynamics results for the pressure and internal energy as obtained from Eqs. (6) and (7), respectively. Columns 3 and 6 give the values found by applying the approximation $g_0(r) \approx g(r)$. Columns 4 and 7 give the molecular-dynamics (MD) results (Ref. 8); the error bounds here are ± 0.05 . The results obtained by using the solution of the Percus-Yevick (PY) equation for $g(r)$ (Ref. 7) are given in columns 5 and 8.

Thermodynamic state		$\beta p/\rho$			$-\beta\Delta E/N$		
$\rho\sigma^3$	$(\beta\epsilon)^{-1}$	This work	MD	PY	This work	MD	PY
0.85	0.88	1.82	1.64	3.17	6.77	6.75	6.61
0.85	0.786	1.23	0.99	2.97	7.70	7.70	7.51
0.85	0.719	0.69	0.36 ^a	2.82	8.52	8.51	8.28
0.85	1.128	2.82	2.78	3.57	5.08	5.05	4.98

^aMolecular-dynamics results for $\rho\sigma^3=0.85$, $(\beta\epsilon)^{-1}=0.72$, predict $\beta p/\rho=0.43$ (Ref. 8).

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BOUNDS, SUCCESSIVE APPROXIMATIONS, AND THERMODYNAMIC LIMITS FOR DISTRIBUTION FUNCTIONS, AND THE QUESTION OF PHASE TRANSITIONS FOR CLASSICAL SYSTEMS WITH NON-NEGATIVE INTERACTIONS

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It is shown rigorously that, for systems with non-negative interactions and integrable Mayer f bonds (e.g., hard spheres), distribution functions and the thermodynamic ratio ρ/z exist in the limit $V \rightarrow \infty$, and are analytic functions of the activity z , for $z < 1/f$ in the right-hand half-plane, with f the absolute value of the integral of the f bond. Heuristic arguments then indicate that these functions are continuous in z for all $z < \infty$. This would mean that no Ehrenfest phase transitions are possible for such systems.

The problem of bounds for thermodynamic and distribution functions and the existence of thermodynamic limits has aroused considerable interest in recent years.¹ While the problem has been treated successfully for simple thermodynamic functions such as pressure or the thermodynamic ratio ρ/z (with z the activity and ρ the number density),² existence of limits for distribution functions has not been proven even at low activities. On the other hand, the question of the thermodynamic significance of singularities obtained from approximate theories for non-negative interactions,³ and of discontinuities observed in computer calculations,⁴ is still unresolved.

In this note, we report the following rigorous results for systems with non-negative interactions: (I) For z real and non-negative, the thermodynamic limits of distribution functions and of the thermodynamic ratio (if they exist) are bounded above and below by the limits of two sequences, monotone decreasing and monotone increasing, respectively. The members of these sequences can be calculated successively in a straightforward manner, thus providing successively better and better approximations to these functions. (II) For z complex in a domain D^* bounded on the right by the semicircle $z < 1/f$ (with f the absolute value of the integral of the Mayer f bond), and on the left by the imaginary axis and the semicircle $z < 1/ef$ (the Groeneveld lower bound for radii of convergence of cluster expansions⁵), both bounds are regular functions of z . Finally, we show (III) for z within D^* both bounds are equal, thus the thermodynamic limits exist and are regular in z . The physically interesting part of D^* , which includes the part $|z| < 1/f$ of the non-negative real z axis, is considerably larger than that defined by the Groeneveld bound. Following these proofs, we present some heuristic arguments for existence of these limits for all $0 \leq z < \infty$, and their continuity in z . The latter is tantamount to nonexistence of Ehrenfest⁶ phase transitions for the systems under consideration, e.g., hard spheres.

The N -particle interaction potential is written⁷

$$U_N(\underline{N}) \equiv U_N(1, 2, \dots, N) \equiv U_N(\vec{r}_1, \dots, \vec{r}_N) = \sum_{1 \leq i < j \leq N} U_{ij}; \quad U_{ij} = U_2(\vec{r}_{ij}). \quad (1)$$

We now define Boltzmann factors and f bonds:

$$v_N(\underline{N}) \equiv \exp[-U_N(\underline{N})/kT] = \prod_{1 \leq i < j \leq N} v_{ij}, \quad v_{ij} \equiv \exp(-U_{ij}/kT), \quad f_{ij} \equiv v_{ij} - 1. \quad (2)$$