Inherent pair correlation in simple liquids

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This paper is dedicated to the proposition that liquids possess an inherent packing structure which is determined by their collection of potential energy minima. To reveal the inherent structure in a given thermodynamic state, it is necessary to subject the dynamical system to steepest-descent "quenches" that remove thermal motion and distortion and leave the system in the nearest mechanically stable arrangement. Such a program has been carried out via molecular dynamics simulation on an argon-like system containing 108 atoms. Two thermodynamic states at the same reduced density ($\rho^* = 1.0$) were considered, one just above the melting temperature T_m^* and one at approximately $3.5\ T_m^*$. Although the pair correlation functions $g(r)$ in these thermodynamic states differed considerably, those produced by the corresponding sets of quenches $g_q(r)$ were virtually identical. The implied inherent structure common to both states appears to be best described in terms of highly defective face-centered-cubic crystalline configurations.

I. INTRODUCTION

Understanding liquids is a formidable problem. In an effort to introduce some simplification we have proposed and pursued an approach which isolates static packing properties of the atoms or molecules involved from effects attributable to thermal excitation.[1-6] The static packings are simply those particle arrangements for which all forces vanish, i.e., minima of the potential energy Φ. Barring exceptional cases of zero measure, any N-particle configuration represented by the multidimensional vector r can uniquely be assigned to a nearby potential minimum; the connection is established by solving the steepest-descent equation

$$\dot{\mathbf{r}} = -\nabla\Phi \tag{1.1}$$

with r as an initial condition. Equation (1.1) moves the system monotonically downward on the Φ hypersurface toward the relevant minimum.

If classical dynamics is an appropriate description, the time evolution of the many-particle system will be given by a continuous vector r(t). Equation (1.1) provides a mapping of r(t) onto a piecewise constant vector $\mathbf{r}_q(t)$, the configurations of mechanically stable packing relevant to the given dynamical motion at each instant of time. If the conserved total energy is high (as in the thermodynamically stable liquid phase), $\mathbf{r}_q$ will display frequent jump discontinuities as the system explores the configuration space diffusively. By contrast, $\mathbf{r}_q$ could be invariant if the temperature were so low that the system were trapped in the neighborhood of a single minimum.

Our purpose in the present study has been to examine the effect of steepest-descent quenching from r(t) to $\mathbf{r}_q(t)$ on the pair correlation function for a simple argon-like model. The pair correlation function is a natural object for attention because of its relationship with x-ray and neutron diffraction experiments on the one hand, and because it vividly shows the structure-revealing effect of the quenching on the other hand.

Modelistic details and the computational procedure are outlined in Sec. II. Results appear in Sec. III. We discuss the implications of those results in a final Sec. IV.

II. COMPUTATIONAL PROCEDURE

Our dynamical system and the numerical details involved in integrating its classical equations of motion have been discussed in prior publications.[5,6] We employ $N = 108$ structureless particles in a cubical unit cell with periodic boundary conditions. The potential energy Φ consists of central pair components:

$$\Phi = \sum_{i<j=1}^{N} v_0(r_{ij}). \tag{2.1}$$

Pair potential v_0 has the following functional form:

$$v_0(r) = A\,(r^{-12} - 1)\exp[1/(r-a)] \quad (0 < r < a), \tag{2.2}$$
$$= 0 \quad (a \leqslant r),$$

with

$$A = 8.805\ 977, \quad a = 1.652\ 194. \tag{2.3}$$

In spite of the fact that v_0 changes functional form across $r = a$, derivatives of all orders remain continuous at that point.

The numerical values (2.3) selected for A and a cause v_0 to share three basic properties with the reduced Lennard-Jones function

$$v_{\text{LJ}}(r) = 4(r^{-12} - r^{-6}); \tag{2.4}$$

specifically we have for both functions ($\alpha = 0$,LJ)

$$v_\alpha(1) = 0, \quad v_\alpha(2^{1/6}) = -1, \quad v_\alpha'(2^{1/6}) = 0. \tag{2.5}$$

Therefore we can regard v_0 as a smoothly cut-off version of v_{LJ}, a feature which provides substantial numerical advantage. In the present application the cutoff distance a is sufficiently small so that with the given periodic boundary conditions particle i can only interact with the nearest image of particle j.

In order to represent interactions in real substances the interaction potential requires energy (ϵ) and length (σ) rescaling

$$\epsilon v_\alpha(r/\sigma). \tag{2.6}$$

Values of these parameters appropriate for argon (originally selected for use with v_{LJ}) are:

$$\epsilon = k_B \times 120 \text{ K} = 1.6565 \times 10^{-14} \text{ erg}, \quad \sigma = 0.34 \text{ nm}. \tag{2.7}$$

When these are supplemented by m, the mass of one argon atom (6.6423×10^{-23} g), the fundamental time unit turns out to be

$$\tau = \sigma(m/\epsilon)^{1/2} = 2.1530 \text{ ps}. \tag{2.8}$$

Needless to say, our numerical work has been carried out in reduced units for which ϵ, σ, m, and τ all have numerical value unity.

The present study has been restricted to reduced density

$$\rho^* = 1.0. \tag{2.9}$$

At this density the absolute minimum of potential energy Φ is achieved when the 108 particles are arranged in a face-centered cubic (fcc) crystal whose principal directions are aligned with the sides of the cubical box. The value of Φ at this perfect-crystal absolute minimum varies with ρ^*, but the choice (2.9) yields the lowest possible value; it therefore corresponds to the crystal at zero pressure and temperature. In this condition the potential energy per particle is

$$\phi \equiv \Phi / N = -6.0000, \tag{2.10}$$

indicative of the fact that at $\rho^* = 1.0$ only nearest neighbors have interactions with significant magnitude.

Molecular dynamics runs were created at two distinct reduced temperatures,

$$T^* = 2.110, 6.453. \tag{2.11}$$

Both of these states are fluid. The former is only slightly above the melting temperature that was previously determined for this model at the given density

$$T_m^*(\rho^* = 1.0) \equiv 1.85. \tag{2.12}$$

The latter is clearly in a very hot, compressed state.

Numerical integration of the Newtonian equations of motion utilized the fifth-order Gear algorithm[7] with a time step in reduced units

$$\Delta t = 0.001 \ 25. \tag{2.13}$$

Each of the two runs spanned 10^4 time steps (equivalent to 27 ps for argon), and represented extensions of well-equilibrated previous runs at virtually the same temperatures. Total energy remained constant to high accuracy during each run without the need for momentum scaling adjustments.

Without actually disturbing the dynamical integration routine, each molecular dynamics run was "quenched" every $100 \, \Delta t$ to locate the configuration of the nearest Φ minimum. This was accomplished using a combination of Newton's method and the conjugate-gradient method[5,6] to produce the relevant asymptotic solution to Eq. (1.1). By including the initial and final states of the dynamical sequence this procedure created 101 minima per state on which the analysis of the following Sec. III was based.

Location of the configurations of relative Φ minima is by far the most demanding part of the numerical task. It is this feature which has limited our study to systems with only 108 particles.

TABLE I. Properties of the 108-particle argon-like system at $\rho^* = 1.0$.

T^*	2.110	6.453
$\langle \phi \rangle$	-2.1638	1.8833
R_1	1.04	0.98
$g(R_1)$	2.69	2.09
r_1	1.47	1.45
$g(r_1)$	0.58	0.74
R_2	1.95	1.96
$g(R_2)$	1.27	1.15
$n(r_1)$	13.0	12.3

III. RESULTS

Table I lists several properties that have been determined as averages for the two dense fluid states studied. Included are the thermal mean values $\langle \phi \rangle$ of the potential energy per particle for those two thermodynamic conditions; these latter fall accurately on the fluid branch of the corresponding $\rho^* = 1.0$ curve that was determined earlier[5] for the temperature dependence of this property.

Figures 1 and 2 show the pair correlation functions $g(r)$ for the two temperatures. On account of the small size of the system, it is only feasible to show these functions for reduced distances less than about 2.45, for otherwise the periodic imaging would intrude. Nevertheless, enough detail is present to establish the existence of reasonably well-defined first and second peaks. The curves shown in Figs. 1 and 2 have just the expected shapes for an argon-like model, with increasing temperature causing a reduction in amplitude of oscillations about the random-distribution value unity.

Table I provides the distances R_1, r_1, and R_2, respectively, at which $g(r)$ attains its first maximum, first minimum, and second maximum. The corresponding values of g at these extremal points also appear in the table.
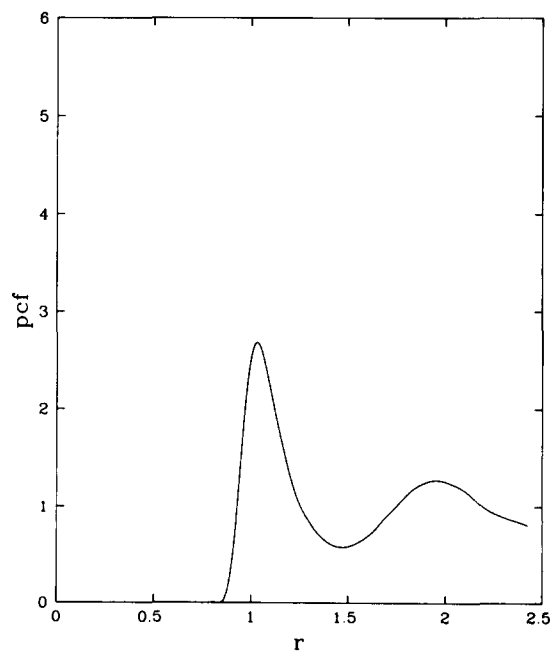

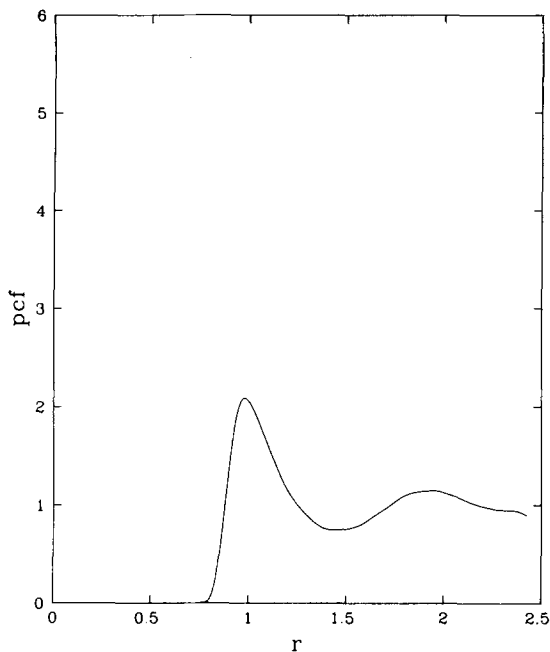FIG. 1. Pair correlation function for the 108-particle system at $\rho^* = 1.0$, $T^* = 2.110$.

FIG. 2. Pair correlation function for the 108-particle system at $\rho^* = 1.0$, $T^* = 6.453$.
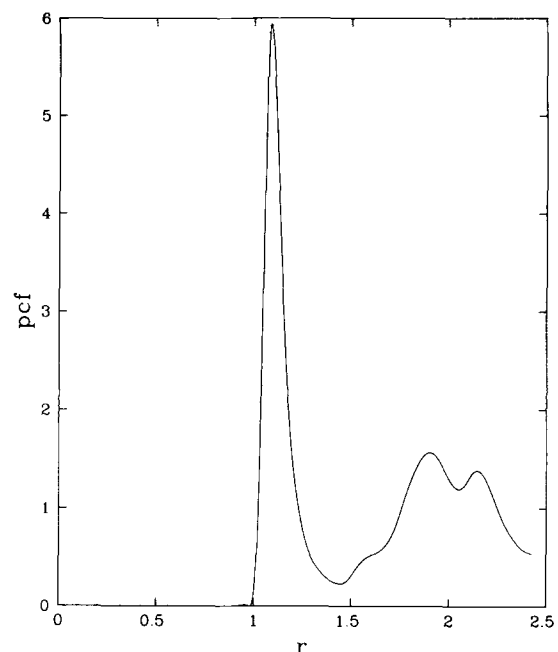
The running coordination number $n(r)$ is defined by the equation

$$n(r) = 4\pi\rho^* \int_0^r s^2 g(s)ds. \tag{3.1}$$

A frequently used definition of the average number of nearest neighbors in a monatomic liquid is $n(r_1)$, for which values are listed in Table I.

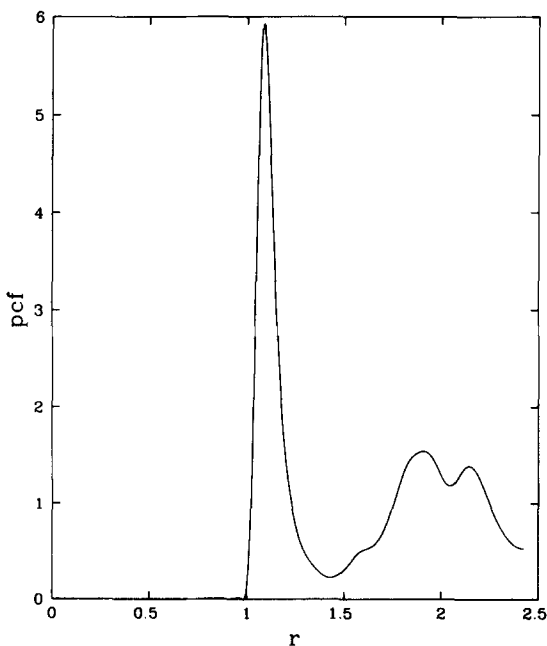The rate at which the 108-particle system undergoes

FIG. 3. Pair correlation function for stable packings generated by quenching the $T^* = 2.110$ liquid.

FIG. 4. Pair correlation function for stable packings generated by quenching the $T^* = 6.453$ hot fluid.

transitions between regions belonging to distinct minima is known to be strongly temperature dependent.[5] Nevertheless, the 0.27 ps interval between successive quenches is expected to be sufficient at both temperatures to permit many intervening transitions. Indeed this was found to be the case; by monitoring the values ϕ_q of ϕ after each quench it was observed that the same minimum was never encountered twice in a row during either molecular dynamics run. The absolute minimum ϕ_q value -6.0000 [Eq. (2.10)] never appeared during either case, although previous experience[5,6] indicates that it can occur very infrequently in quenching from stable fluid states. The distributions of ϕ_q values for the two cases were similar to one another and to previous determinations. The most probable values cluster near -5.35, and the distributions are skewed to the low (more negative) direction.[5,6] This last observation is consistent with proper uniform sampling of the available collection of particle packings.

Figure 3 (for the $T^* = 2.110$ state) and Fig. 4 (for the $T^* = 6.453$ state) present radial distribution functions $g_q(r)$ for the two sets of quenches. Each curve represents an average over the 101 configurations generated for that case. Two striking observations emerge. First, the quenching produces a remarkable enhancement of structure. Second, the results

TABLE II. Properties of quenches prepared from the fluid at $\rho^* = 1.0$.

T^*(initial)	2.110	6.453
$\langle \phi_q \rangle$	-5.3693	-5.3563
R_{1q}	1.09	1.09
$g_q(R_{1q})$	5.93	5.94
r_{1q}	1.43	1.44
$g_q(r_{1q})$	0.22	0.23
$n_q(r_{1q})$	12.81	12.86

are virtually identical to one another in contrast to the substantially different prequench functions $g(r)$ in Figs. 1 and 2. Table II contains values of $\langle \phi_q \rangle$, as well as $R_{1q}, r_{1q}, g_q(R_{1q}), g_q(r_{1q})$, and the quench-state coordination number $n_q(r_{1q})$ that is defined as in Eq. (3.1).

IV. DISCUSSION

Rahman, Mandell, and McTague[8] have utilized the molecular dynamics simulation method to study a 500-particle amorphous system of Lennard-Jones particles. It is worth remarking that their pair correlation function closely resembles those appearing here in Figs. 3 and 4. In particular they also observe a "split second peak" whose two components flank reduced distance 2.0, an attribute which has occasionally been regarded as a hallmark of the amorphous state for monatomic materials.[9,10] Differences between their result and ours, while small, probably stem from a combination of the following:

(i) v_{LJ} differs from the pair interaction v_0 employed in our work, particularly at long range;

(ii) a low but nonvanishing temperature prevailed in the Rahman, Mandell, and McTague study ($T^* = 0.108$), while their reduced density was slightly smaller than ours (0.95 vs 1.00 here);

(iii) only a single amorphous sample was considered (possibly vibrating around a single potential energy minimum), whereas we have averaged over many distinct minima; and

(iv) their system ($N = 500$) was considerably larger than ours ($N = 108$).

It should be mentioned that Wendt and Abraham[11] have also generated amorphous-state Lennard-Jones pair correlation functions, by the Monte Carlo simulation technique. Their low-temperature results likewise display a split second peak.

The first four coordination shells in the fcc crystal have relative distances (coordination numbers) given by 1 (12), $2^{1/2}$ (6), $3^{1/2}$ (24), 2 (12). These magnitudes correlate rather well with the positions and sizes of the first peak, the shoulder, and the two parts of the split second peak shown in both Figs. 3 and 4. This strongly suggests that the majority of the relative potential minima contributing to our quenched amorphous states can be described as defective fcc structures. The widths (and resultant overlappings) of the peaks in $g_q(r)$ would then be explained as frozen-in strains induced by the defects. This presumption has been directly supported by examining stereo photographs of selected packings generated during this work which in fact show defect-containing fcc structures. It is also supported by the fact that $r_{1q} = 1.09$ in Table II is slightly less than the expected $2^{1/16} = 1.1224...$for a perfect fcc lattice at $\rho^* = 1.0$; the mean density of amorphous packings at zero pressure has been determined to be $\rho^* = 0.97$ for the present model[6] implying that nearest neighbors would be forced into slightly closer contact when compressed to the given density 1.0. We also take note of Abraham's claim[12] that amorphous states of the Lennard-Jones model resemble "distorted fcc packing."

That Rahman, Mandell, and McTague failed to identify a shoulder on the small-r side of their split second peak[8] may be due primarily to their use of nonzero temperature.

An important unsolved problem is whether *all* potential energy minima can uniquely be described as defect-containing crystals. If the answer were affirmative, this would simplify enormously the enumeration task for those minima.

Comparison of entries in Tables I and II shows the possible danger of interpreting experimental (or simulation) pair correlation functions in structural terms. The mean numbers of nearest neighbors $n(r_1)$ for the two temperatures are substantially different in Table I, perhaps inducing the viewer to conclude that the "structures" of the cool and of the hot fluids were rather distinct. Yet both appear to quench to essentially the same collection of inherent structures. The differences are due primarily to the degree of vibrational excitation *within* the regions around relative minima, not to thermally induced population shifts *between* those regions.

It is this latter point which constitutes our major conclusion. It suggests that understanding of, and theory for, the liquid state of simple monatomic substances could profitably be based on the existence and relevance of underlying inherent structures as we have defined them. In particular this may lead to a new approach to predicting pair correlation functions at arbitrary temperatures. Transport theory might also benefit from this viewpoint, and indeed Zwanzig has begun exploratory investigations along these lines.[13] To strengthen the case it is desirable to carry out the same type of study as that reported here for a variety of interaction potentials.

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