COMMUNICATIONS

A scaling principle for the dynamics of density fluctuations in atomic liquids

Thomas Young and Hans C. Andersen
Department of Chemistry, Stanford University, Stanford, California 94305

On the basis of the fully renormalized kinetic theory of equilibrium classical atomic fluids, we conjecture that different fluids with very different interatomic potentials might have very similar dynamical density fluctuations if they have similar static pair correlation functions. Molecular dynamics simulations are presented that provide support for this conjecture. This suggests that in order to understand how the interatomic potential of a liquid determines its dynamical properties, it is worthwhile focussing separately on the two questions of how the potential affects the pair correlation function and how the pair correlation function affects the dynamics. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1553757]

I. INTRODUCTION

Much research on the dynamics of liquids, especially molecular dynamics simulation studies, is concerned with understanding the relationship between the interatomic potential and the dynamic correlation functions and transport properties of liquids. Accordingly, molecular dynamics computer simulations have been performed with a variety of different types of potentials.[1–4] On the other hand, several formal kinetic theories[5–9] have expressed the dynamics of a fluid in terms of the static correlation functions of the fluid with no direct reference to the interatomic potential. In addition, Dzugutov[10] (see also Hoyt *et al.*[11]) has presented an empirical scaling principle that allows the self diffusion coefficient of an atomic liquid to be estimated accurately from the density and pair correlation function of the liquid without a knowledge of the potential.[12]

The fact that a formally exact kinetic theory can be expressed in terms of the static correlation functions suggests the possibility that different liquids that have similar static correlation functions might have similar dynamical properties, even if their potentials are quite different. It also suggests that in order to understand the effect of the potential on the dynamics, it might be better to consider the following two questions separately: (1) How does the potential affect the static correlation functions? (2) How do the static correlation functions affect the dynamics? The first question is a standard question in equilibrium statistical mechanics, about which much is known. The second question can be addressed using renormalized kinetic theory without consideration of the potential.

In this paper, we confirm that this may be a useful approach. We present an approximate scaling principle that postulates a relationship between the dynamics of systems with very similar static correlations but very different potentials. We also present empirical support for this approximate scaling principle.

II. EXACT AND APPROXIMATE SCALING RELATIONSHIPS

We consider a one component classical atomic fluid, regarded as a set of N interacting point particles, each of mass m, in volume V, to which classical mechanics and classical statistical mechanics apply.

Let $n(\mathbf{R}) = \Sigma_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{R})$ be the microscopic density of particles at position $\mathbf{R}$, where $\mathbf{r}_i$ is the position of particle i. The static correlation functions of interest for the system are equilibrium ensemble averages of products of this density, namely $\langle n(\mathbf{R}_1)...n(\mathbf{R}_m)\rangle$. In particular, $\langle n(\mathbf{R}_1)n(\mathbf{R}_2)\rangle = n\delta(\mathbf{R}_1 - \mathbf{R}_2) + n^2 g(\mathbf{R}_1 - \mathbf{R}_2)$, where $n = N/V$ and g is the usual pair correlation function. Its Fourier transform is simply related to the usual structure factor $S(k)$.[1] Let $f(\mathbf{R},\mathbf{P},t) = \Sigma_{i=1}^{N} \delta(\mathbf{R} - \mathbf{r}_i(t))\delta(\mathbf{P} - \mathbf{p}_i(t))$ be the microscopic density at time t of particles at a point, $\mathbf{RP}$, in single particle phase space. The dynamic correlation function $\langle f(\mathbf{R}_1,\mathbf{P}_1,t_1)f(\mathbf{R}_2,\mathbf{P}_2,t_2)\rangle$ is simply related to the usual intermediate scattering function $F(k,t)$ and the longitudinal and transverse current autocorrelation functions. Other dynamic correlation functions of interest are the incoherent intermediate scattering function $F_s(k,t)$, the velocity autocorrelation function, and the self longitudinal current autocorrelation function (which includes the single particle contributions to the longitudinal current autocorrelation function).[1]

For such a fluid it is straightforward to prove the following exact scaling principle: Suppose two equilibrium atomic fluids have the same number density but possibly different atomic masses and different temperatures. If all the multipoint static correlation functions of the density are the same for both systems, then the two fluids have identical dynamic correlation functions provided they are expressed in terms of scaled momenta $\widetilde{\mathbf{P}} = \mathbf{P}/(mk_BT)^{1/2}$ and scaled time $\widetilde{t} = (mk_BT)^{1/2}t$. (Here, k_B is Boltzmann's constant.)

The proof of this theorem makes use of the fact that the

assumptions about the static correlation functions of the two fluids are strong enough to imply that the total potential energy functions of the two systems are related by $U_1(\mathbf{r}^N)/k_B T_1 = U_2(\mathbf{r}^N)/k_B T_2 + (\text{constant})$, where the subscripts 1 and 2 refer to the two systems.

We now make the following conjecture, which is an approximate scaling principle: Suppose two equilibrium atomic fluids have the same number density but possibly different particle masses and different temperatures. If the static *pair* correlation functions for the two systems are very similar, their dynamic correlation functions, when scaled as discussed in the exact scaling principle, are very similar, *even though their potentials may be very different.*

The conjecture is motivated by the fact that formally exact renormalized kinetic theories can be derived that express the dynamics of the correlation functions entirely in terms of the static correlation functions of the density, without explicit reference to the potential. In order for the conjecture to be true, presumably both of the following statements would have to be true. (1) The dynamics are not very sensitive to the static correlation functions. (i.e. changes in the potential that are large will lead to only small changes in the dynamics if they cause only small changes in the static structure.) (2) Either the static pair correlation function is the dominant correlation function for determining the dynamics, or the fact that the static pair correlation functions of the two systems are similar also implies that the higher correlation functions are also similar.

This is merely a conjecture, but one that can clearly be tested. We shall give examples below where it holds quite well.

III. TESTS OF THE CONJECTURE

As part of a systematic study of dynamics in fluids, we have performed molecular dynamics simulations of the Lennard-Jones fluid at one density for a variety of temperatures. For comparison, at each temperature we also performed simulations of a system whose interatomic potential is the repulsive part of the Lennard-Jones potential.[13]

The Lennard-Jones potential is of the form

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

In the molecular dynamics calculations for the Lennard-Jones potential, the potential actually used was one that was truncated at a cutoff distance of $r = 2.5\sigma$ and shifted upward to make it continuous at the cutoff.

$$u_{LJ}(r) = u(r) - u(2.5\sigma) \quad \text{for } r \leq 2.5\sigma$$
$$= 0 \quad \text{for } r \geq 2.5\sigma.$$

We shall refer to this as the LJ potential. We also performed calculations using a potential that is the repulsive part of the Lennard-Jones potential.

$$u_{RLJ}(r) = u(r) - u(2^{1/6}\sigma) \quad \text{for } r \leq 2^{1/6}\sigma$$
$$= 0 \quad \text{for } r \geq 2^{1/6}\sigma.$$

Unlike the LJ potential, this potential is nonnegative and has no attractive forces. It is also of much shorter range than the LJ potential. The fundamental units are σ for distance, ϵ for
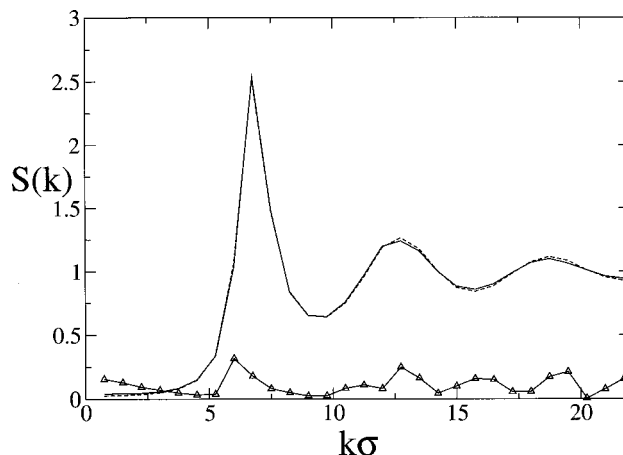

FIG. 1. The static structure factor $S(k)$ as a function of $k\sigma$ for the LJ system at $T^* = 1.000$ (upper solid curve) and the RLJ system at $T^* = 0.723$ (upper dashed curve). These two curves are barely distinguishable in this figure. The lower curve with triangle data points is a plot of ten times the absolute value of the difference between the two upper curves.

energy, and m, the particle mass, for mass. The corresponding unit of time is $\tau = (m\sigma^2/\epsilon)^{1/2}$. The temperatures quoted below are reduced temperatures $T^* = k_B T/\epsilon$.

In each simulation, the system contained $N = 500$ particles in a cubic box with periodic boundary conditions. For all simulations reported here, the reduced density $\rho^* = N\sigma^3/V$ was 0.8500. The velocity form of the Verlet algorithm[14] was used to integrate the equations of motion, with a time step of 0.008τ. For each potential used and each temperature, the system was thoroughly equilibrated before generating data for the calculation of time correlation functions. For each temperature, density, and potential, 100 runs were performed, each of duration $5 \times 10^4 \tau$ or $10^5 \tau$, and the correlation functions were averaged over the runs.

At any one temperature, the two potentials lead to similar pair correlation functions and structure factors.[13] Closer examination of the static correlation functions reveals that an LJ system at one temperature has a structure that is more similar to that of an RLJ system at a significantly lower temperature. For example, see Fig. 1, which compares the static structure factors $S(k)$ for the LJ system at $T^* = 1.000$ and the RLJ system at $T^* = 0.723$. At all temperatures for both systems at this density, the oscillations in $S(k)$ are in phase. The major noticeable differences among the curves is the amplitude of the major peak. When an LJ system and an RLJ system have the same amplitude for the first peak, the overall behaviors of the two $S(k)$ curves are very similar.

By comparing the amplitudes of the first peak in $S(k)$ we have found four pairs of systems that have very similar static structure. One pair is LJ at $T^* = 1.000$ and RLJ at $T^* = 0.723$, as mentioned above. The others are: LJ at 0.723 and RLJ at 0.446; LJ at 1.277 and RLJ at 1.000; and LJ at 1.554 and RLJ at 1.277. Within each pair, the two systems have similar structure. Different pairs have different static structures.

Figure 2 compares $F_s(k,t)$ for a wave vector of $k = 6.75\sigma^{-1}$ for the eight systems studied, when plotted versus reduced scaled time $\tilde{t}^*$. [Scaled time is defined above as $\tilde{t} = (mk_B T)^{1/2}t$. Reduced scaled time is the dimensionless ver-
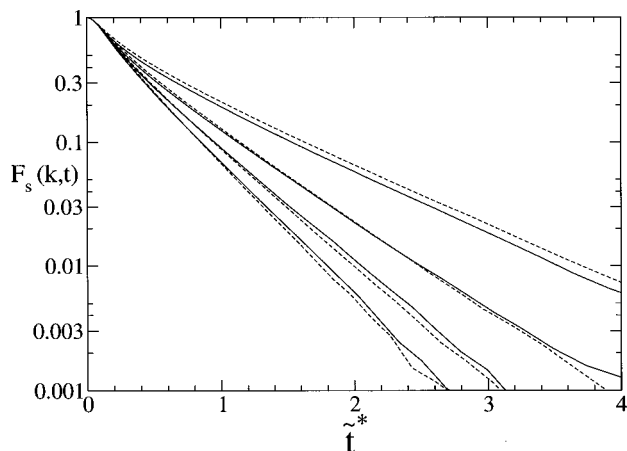
FIG. 2. The incoherent intermediate scattering function $F_s(k,t)$, for $k = 6.75/\sigma$ as a function of scaled reduced time $\tilde{t}^*$ for the eight systems studied. The solid curves are for the LJ system at reduced temperatures of 1.554 (bottom curve), 1.277 (second from bottom), 1.000 (third from bottom), and 0.723 (top). The dashed curves are for the RLJ system at reduced temperatures of 1.277 (bottom), 1.000 (second from bottom), 0.723 (third from bottom), 0.446 (top curve). Each pair of closely neighboring curves corresponds to a pair of systems with very similar structure factors.

sion of this for the usual Lennard-Jones units: $\tilde{t}^* = (T^*)^{1/2}t^*$, where the reduced time is $t^* = t/\tau$.] In each case, the pairs of states with similar structure have very similar time dependence of $F_s(k,t)$. In this graph, the maximum difference between the curves for states of similar structure is approximately 0.02 for the three highest temperature pairs and 0.03 for the lowest temperature pair. Similar results are obtained for all wave vectors.

Figure 3 gives the analogous results for the $F(k,t)$. This agreement with the approximate scaling principle holds for the intermediate scattering function only for larger wavevectors.

Figure 4 compares the velocity autocorrelation functions for one pair of corresponding states for short times. [The function plotted corresponds to the function denoted $\psi(t)$ by Boon and Yip.[1]] In contrast with the results above for F and F_s, the velocity autocorrelation functions are generally quite different for pairs of states with similar structure. Neverthe-

FIG. 4. The velocity autocorrelation function, divided by its zero time value, as a function of reduced scaled time for short times $\tilde{t}^* \leqslant 0.3$ for the two systems in Fig. 1. The curves are also noticeably different for $0.3 \leqslant \tilde{t}^* \leqslant 0.9$, after which both curves are zero within the statistical error.

less, the self diffusion coefficients, appropriately scaled, which vary by a factor of two for this range of states, are in close agreement for pairs of similar states (2% difference for the three higher temperature pairs and 6% difference for the lowest temperature pair).

The velocity autocorrelation function is equivalent to the self longitudinal current autocorrelation function for zero wavevector. Figure 5 compares the self longitudinal current autocorrelation functions for the same pair of systems but for a nonzero value of the wave vector. At very short times ($t^* < 0.3$, not shown in this figure) there are significant differences similar to those seen for zero wave vector, but for later times the curves are very similar.

IV. DISCUSSION

On the basis of the data presented here and similar data to be presented later, we state the following generalizations for this type of comparison of LJ and RLJ systems. The
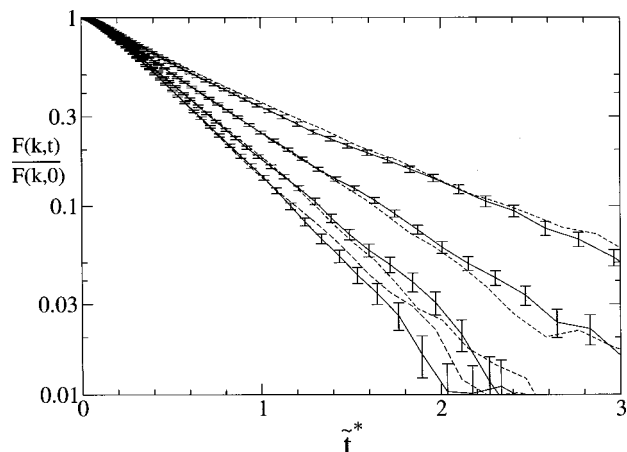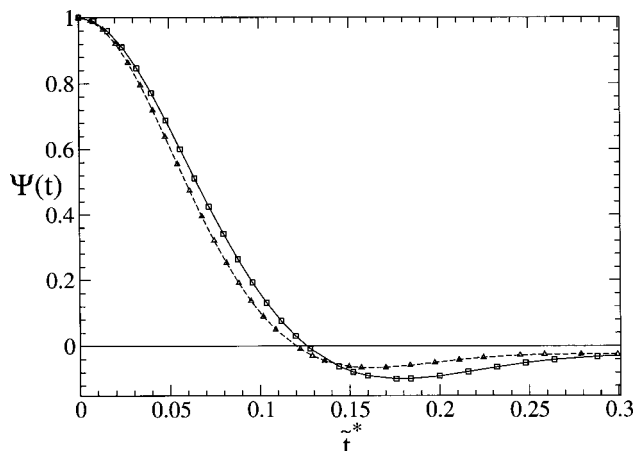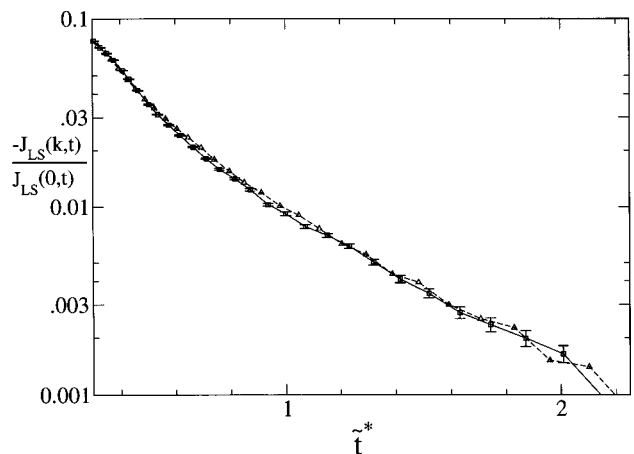

FIG. 3. The intermediate scattering function $F(k,t)$, divided by its zero time value, as a function of scaled reduced time $\tilde{t}^*$ for the eight systems studied. See the caption of Fig. 2 for details.

FIG. 5. The self longitudinal current correlation function, $J_{LS}(k,t)$, divided by its zero time value and multiplied by -1, as a function of reduced scaled time for $\tilde{t}^* \geqslant 0.3$ for the two systems in Fig. 1. For $\tilde{t}^* < 0.3$, the curves are different, similar to what is shown in Fig. 4 for a closely related function, but the short time behavior has been omitted in order to provide a clearer demonstration of the similarity of the curves for the time range presented.

similarity in the dynamics is strongest for $F_s(k,t)$ for all wavevectors and times, $F(k,t)$ for wavevectors of $6.75/\sigma$ and above for all times, the longitudinal current correlation functions at longer times (scaled reduced times greater than about 0.3), the transverse current autocorrelation function for the smallest wave vector studied, and the self-diffusion coefficient. The similarity is weakest or nonexistent for $F(k,t)$ for smaller wavevectors, the longitudinal current autocorrelation functions for short times (reduced scaled times less than about 0.3), and the transverse current autocorrelation function for all but the smallest wavevector.

For each pair of systems being compared, the differences between the pair correlation functions of the two systems are small but they are not zero. Many of the differences that are observed for the dynamics of corresponding states can be understood at least qualitatively on the basis of the small differences that exist in the pair correlation functions and on the basis of the renormalized kinetic theory.

For example, a major difference between the structures of the states in a pair is that the static structure factor $S(k)$ at small wavevector is larger for the system with attractive forces. The value at zero wavevector is related to the compressibility. The difference in the compressibility makes the speed of sound of the two systems very different. The intermediate scattering function contains oscillations associated with longitudinal sound waves, and the oscillations are different for the two different systems because of the different scaled sound speeds. This accounts qualitatively for much of the discrepancy between the $F(k,t)$ results for the two systems at small k.

More extensive data, comparisons, and interpretations will be presented in a later publication.

[1] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
[2] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
[3] U. Balucani and M. Zoppi, *Dynamics of the Liquid State*, 1st ed. (Oxford, New York, 1994).
[4] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford, New York, 1989).
[5] E. P. Gross, Ann. Phys. (N.Y.) **69**, 42 (1972).
[6] G. F. Mazenko, Phys. Rev. A **9**, 360 (1974).
[7] C. D. Boley, Phys. Rev. A **11**, 328 (1975).
[8] G. F. Mazenko and S. Yip, in *Statistical Mechanics. Part B: Time-Dependent Processes*, edited by B. J. Berne (Plenum, New York, 1977).
[9] H. C. Andersen, J. Phys. Chem. B **106**, 8326 (2002).
[10] M. Dzugutov, Nature (London) **381**, 137 (1996).
[11] J. J. Hoyt, M. Asta, and B. Sadigh, Phys. Rev. Lett. **85**, 594 (2000).
[12] In contrast, most other kinetic theories express dynamical properties in terms of both the interatomic potential and the static structure or are constructed solely for one potential, namely the hard sphere potential.
[13] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[14] W. C. Swope, H. C. Andersen, P. H. Behrens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982).