

Addendum to "Density fluctuations in liquid rubidium"

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We performed molecular-dynamics simulations of liquid rubidium and the Lennard-Jones fluid at several densities and temperatures, and of a system whose pair potential is the repulsive core of the rubidium potential. In all cases, propagating density fluctuations occurred in the rubidiumlike systems at much shorter wavelengths than in the Lennard-Jones system. This indicates that the repulsive part of the pair potential is the dominant factor in determining the relaxation of short-wavelength density fluctuations.

It was shown in Ref. 1 that the density fluctuations in liquid Rb can be accurately reproduced by a molecular-dynamics simulation if the pair potential of Price *et al.*² is used to represent the effective interactions of the Rb ions. In this note we discuss the results of two sets of molecular-dynamics calculations which extend the results of Ref. 1 and which provide new insights into the dynamics of collective modes in liquids.

Liquid Rb has been observed to support sound modes with wavelengths as small as $1\frac{1}{4}$ times the mean distance between neighboring particles.¹ This is to be contrasted with the situation for the rare-gas liquids³ and for the Lennard-Jones liquid⁴ where the shortest-wavelength sound modes observed are on the order of 5 times the mean nearest-neighbor distance. The simulations discussed here were undertaken to investigate the relative importance of the density, the temperature, and the pair potential in determining this distinctive difference in the short-wavelength properties of liquid rubidium and the rare-gas liquids.

The first set of calculations were performed at Argonne. For this simulation, the potential function employed in Ref. 1, $\phi(r)$, was modified so that only the short-range repulsive part of the potential was used. This truncated potential $\phi_T(r)$ is described by

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$$\phi_T(r) = \begin{cases} \phi(r) + \epsilon, & r < r_{\min} \\ 0 & , r > r_{\min} \end{cases}$$

where $\phi(r_{\min}) = -\epsilon$. The reduced temperature and reduced density, which are listed in Table I for "Truncated Rb", are effectively the same values as used in Ref. 1.

The dispersion of the sound modes is shown in Fig. 1. The main difference between this result and the dispersion of sound modes reported in Ref. 1 is at the high-Q end. When the full potential is used, sound modes are observed for Q's up to 1.2 \AA^{-1} and the slope of the small-Q portion is increased by about 5% over that shown in Fig. 1. The overall effect on the density fluctuations of eliminating the attractive forces is found to be minor, indicating that the attractive part of the pair potential is not an important factor in determining the short-wavelength properties of liquid Rb. There are significant truncation effects on single-particle motions which we discuss later in this note.

TABLE I. Reduced densities n^* and temperatures T^* for the rubidium and Lennard-Jones (LJ) states simulated.

System	n^*	T^*
Truncated Rb	0.9042	0.787
Rb	0.951	0.878
Rb	0.951	1.11
Rb	0.855	1.49
LJ	0.950	0.982
LJ	0.950	1.31

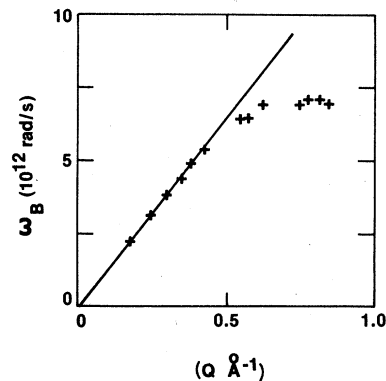


FIG. 1. Dispersion of the sound modes for the truncated rubidium potential with $n^* = 0.9042$ and $T^* = 0.787$.

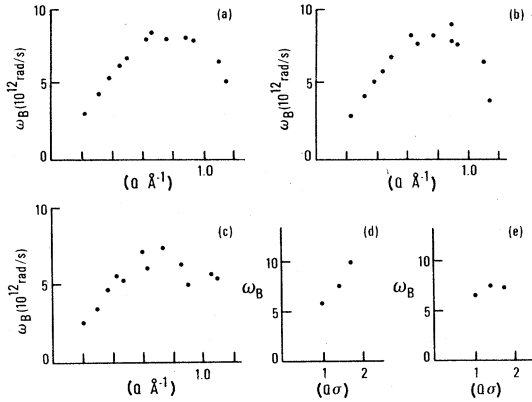


FIG. 2. Dispersion of the sound modes for rubidium and Lennard-Jones states: (a) Rb, $n^*=0.951$, $T^*=0.878$; (b) Rb, $n^*=0.951$, $T^*=1.11$; (c) Rb, $n^*=0.855$, $T^*=1.49$; (d) L-J, $n^*=0.95$, $T^*=0.982$; (e) L-J, $n^*=0.95$, $T^*=1.31$. The scatter in the points is an indication of the accuracy with which ω_B can be estimated, given the system size and duration in our simulation.

The importance of the density and the temperature in determining the dispersion of the sound modes is studied in the second set of calculations. A description of the procedures used in these calculations, which were performed at the National Bureau of Standards (NBS), may be found in Ref. 5. Here the full effective potential of Price *et al.* was used for liquid Rb and the density and temperature were varied from the values used in Ref. 1. Also two Lennard-Jones states were studied to see how density and temperature influenced the short-wavelength sound modes in that system. Recall that Levesque *et al.*⁴ examined the Lennard-Jones

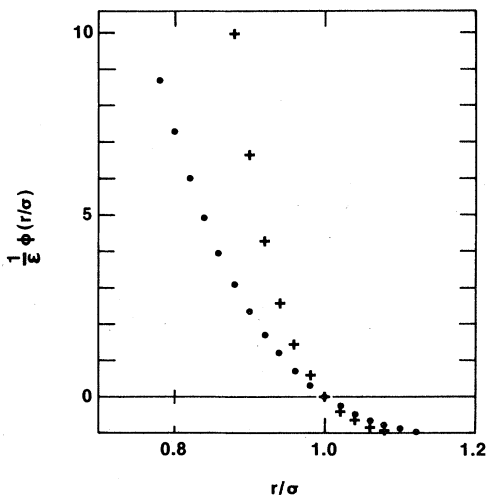


FIG. 3. The repulsive parts of the liquid-rubidium potential (•) and of the Lennard-Jones potential (+). The potentials are in the reduced form $(1/\epsilon)\phi(r/\sigma)$ where ϵ is the well depth and σ is the first zero of ϕ .

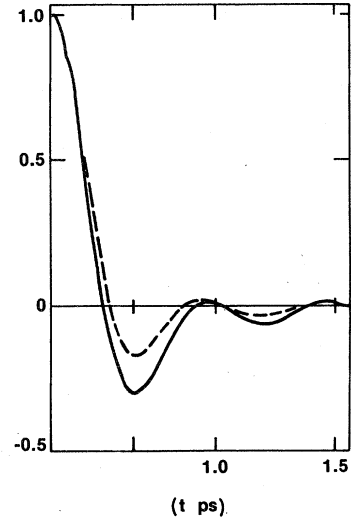


FIG. 4. Normalized velocity autocorrelation functions for the rubidium state of Ref. 1 (—) and for the truncated rubidium state (---). Both functions are normalized to unity at $t=0$.

state with $n^*=0.8442$ and $T^*=0.722$. The reduced densities and temperatures considered by us are listed in Table I. The dispersion of the sound modes for these states is shown in Fig. 2. The qualitative features of the sound dispersion, including the upper limit of observability, are not influenced to any significant extent when the density and temperature are varied over the range of values listed in Table I.

If hydrodynamic region of a fluid is defined in terms of the range of wave vectors for which the fluid is able to support sound modes, our studies show that the upper limit in wave-vector space of the hydrodynamic region of a liquid is mainly determined by the repulsive portion of the pair potential. The rubidium potential is rather softer than is the Lennard-Jones potential as can be seen in Fig. 3 where the repulsive parts of the two potentials are displayed in reduced form. We conclude that the softer core of the rubidium potential leads to the much larger upper limit in wave-vector space for the hydrodynamic region of that fluid.

The single-particle velocity autocorrelation functions for the truncated rubidium state and for the full potential state of Ref. 1 are shown in Fig. 4. The long-time behavior of the velocity autocorrelation function is strongly influenced by the attractive part of the potential. This influence is larger for liquid rubidium than it is for the Lennard-Jones fluid. This can be seen most directly by considering the change in the self-diffusion coefficient which occurs when the attractive forces

are removed. For rubidium, there is a 60% increase in the dimensionless self-diffusion coefficient from 0.028 to 0.048 while for the Lennard-Jones fluid, the increase is less than 20%.⁶

In summary, we have shown that the repulsive part of the pair potential is the major factor which determines the limit of the hydrodynamic region for these liquids while the density, temperature, and the attractive part of the potential are minor

factors. Further, we have shown that the attractive part of the potential has a significant influence on single-particle motions in liquid rubidium and that this effect is substantially larger for liquid rubidium than it is for the Lennard-Jones liquid.

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