Microscopic dynamics in liquid alkali metals

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The structural and dynamical properties of liquid alkali metals near melting are investigated by realistic computer simulations, which support the idea that several important features follow from suitable scaling criteria. The data are found to be in excellent agreement with the recent theories of single-particle dynamics in simple liquids.

Experiments on monatomic liquid metals had in the past a considerable impact on our present understanding of the dynamics of the liquid state. In particular, the pioneering study of liquid Rb by inelastic neutron scattering [1] had in this respect a role comparable with the investigations of liquid argon, the typical "Lennard-Jones" system. Recently, even more detailed neutron measurements have been reported for another alkali metal, namely liquid Cs near the melting point [2]. Besides their direct relevance, these data may provide further information on the effective pair potentials to be possibly adopted in realistic molecular-dynamics (MD) simulations for liquid alkali metals. Second, both the "real" and the MD data may be used as natural benchmarks for the microscopic theories of the dynamics of simple liquids, a test made easier by the fact that these nonphenomenological approaches are nowadays able to predict several important results in a rather simple way. In the present contribution we consider both these aspects, starting from the above-mentioned data for Cs to explore dynamical features valid also for the other alkali metals near their melting point. Liquid lithium is, however, excluded from the very start because of its quantum character.

Empirical evidence that for these systems a sort of "universal" behavior is somehow to be expected is already provided at the equilibrium level. For example, near melting the static structure factors $S(k)$ of liquid Na, K, Rb, and Cs are found to nearly coincide when plotted in terms of the scaled unit k/k_m, where k_m denotes the position of the main peak of $S(k)$ in each system. This sort of "scaling" for the structural properties (noted previously [3] using slightly different recipes) relies on x-ray diffraction data [4], which in the case of liquid Cs are consistent with the neutron measurements of Ref. [2]. When planning a series of simulations in these liquids, the implication to be argued is that the main input quantity, namely a realistic effective pair potential $v(r)$, should also scale. The potential implemented by Price, Singwi, and Tosi [5], which has been tested successfully in the case of liquid Rb [6], appears to be partic-

ularly convenient in this respect. Although no natural units for scaling lengths and energies are *a priori* apparent in $v(r)$, in Fig. 1 we show that the various potentials fall on a single line to a very good approximation if their amplitudes are scaled with the respective well depths ε, and the separations between nuclei measured by the position σ of the first zero of $v(r)$.

Having this in mind, we have performed a series of MD experiments for several liquid alkali metals, starting from liquid cesium at the same thermodynamic state as in Ref. [2], namely at a number density $n = 0.0083$ Å^{-3} and a temperature $T = 308$ K. The values of the parameters of $v(r)$ have been found to be $\varepsilon/k_B = 386$ K and $\sigma = 4.761$ Å. The simulations have been performed in the (N, V, E) ensemble by standard MD programs; as usual,
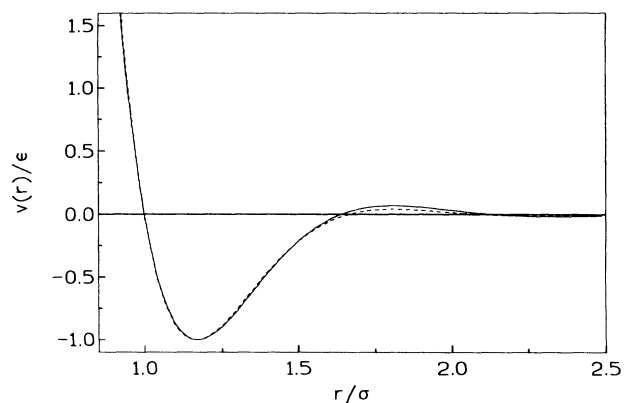

FIG. 1. The effective, density-dependent pair potentials for the liquid alkali metals Na, K, Rb, and Cs near the melting point at a reduced density $n\sigma^3 \approx 0.895$. The potentials have been evaluated according to the recipes of Ref. [5], and scaled with the proper units. The parameters ε (in K) and σ (in Å) are, respectively, 445.6,3.328 (Na); 421,4.115 (K); 402.2,4.408 (Rb); 386.5,4.761 (Cs). The differences between K, Rb, and Cs lie within the thickness of the solid line; the dashed line is the result for Na.
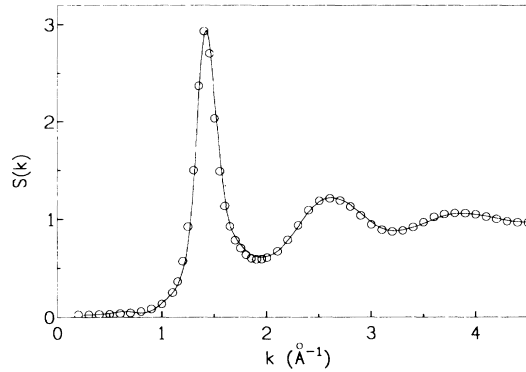
FIG. 2. Comparison between the simulated structure factor $S(k)$ of liquid Cs at 308 K (solid line) and the x-ray data near the melting point (open circles).

both structural and time-dependent properties are obtained by monitoring the configurations of the system after a proper equilibration period. In Fig. 2 we report the comparison between the computed structure factor $S(k)$ and the corresponding x-ray data [4] in liquid Cs. An equally good agreement is obtained for the other alkali metals (Na,K,Rb) [7] between the simulated $S(k)$ and the respective x-ray data reported in Ref. [4]. To explore whether these encouraging results are not just limited to the structural properties, in our simulations we have also evaluated the dynamic structure factor $S(k,\omega)$ for liquid Cs at different wave vectors. A noteworthy feature for these simulations is that the dynamic correlations of liquid Cs span longer times than those of, e.g., liquid Rb, the typical time scale $(M\sigma^2/\varepsilon)^{1/2}$ being 3.07 ps in Cs vs 2.24 in Rb. In Fig. 3 the peak frequencies $\Omega_p(k)$ of the longitudinal current spectra $J_L(k,\omega)=\omega^2 S(k,\omega)$ are successfully compared with the experimental data of Ref. [2]. A similar agreement is present even for the spectral shapes of $S(k,\omega)$ at several wave vectors; a more detailed analysis will be reported elsewhere [7].

Besides the aforementioned "scaling" features, the main conclusion to be drawn from the previous results is

that even for liquid Cs the effective pair potential of Price, Singwi, and Tosi appears to be sufficiently reliable to reproduce satisfactorily the structural and dynamical properties of experimental interest. As a consequence, by means of suitable simulations one expects to obtain realistic results even for quantities which are not immediately accessible by experiment. A time-dependent quantity of this type is, for example, the velocity autocorrelation function (VACF) $\langle \mathbf{v}_1(0)\cdot\mathbf{v}_1(t)\rangle$ which is the simplest probe of single-particle motion in a fluid and is naturally connected to the self-diffusion coefficient D. The VACF has been obtained by a series of independent simulations for Na, K, Rb, and Cs near the melting point at essentially the same reduced density $n\sigma^3 \approx 0.895$. All the findings are reported in Fig. 4, where the VACF's are normalized to their initial values $3k_B T/M$ and the time is measured in units of $\tau=(M\sigma^2/k_B T)^{1/2}$. The results appear to be nearly indistinguishable for the various metals, with some minor deviations in the case of Na due to its slightly higher value of $T^*=k_B T/\varepsilon$ which yields a modest decrease of the oscillatory features [in this respect, the small differences in the reduced $v(r)$ for this element are virtually negligible]. In any case, Fig. 4 gives a clear indication that the "universality" appears to be valid even for

FIG. 4. The velocity autocorrelation functions of the liquid metals Na, K, Rb, and Cs near melting at the reduced temperatures $T^* \approx 0.84$ (Na), 0.81 (K), 0.79 (Rb), and 0.80 (Cs). The proper reduced units have been used (see text). For K, Rb, and Cs all the data are nearly coincident (solid line); the dashed line is the Na result.
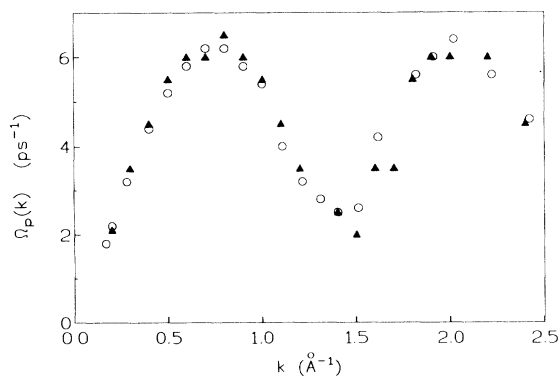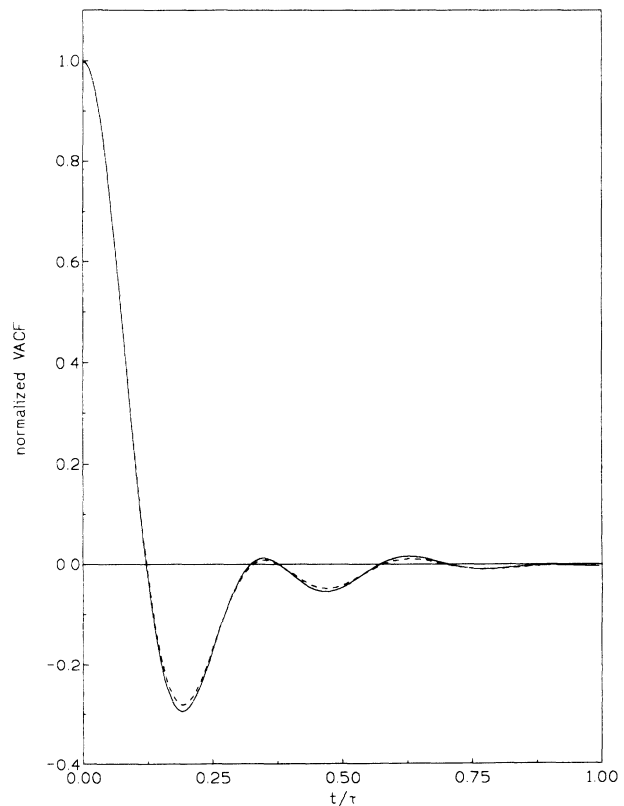

FIG. 3. Comparison between the peak frequency $\Omega_p(k)$ of the longitudinal current spectra in liquid Cs as found in our simulations (open circles) and by neutron scattering (triangles).

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the dynamics. Although other possible choices of the time unit give similar results, the previous one is consistent with the $t = 0$ normalization of the VACF, which implies that in this case the natural energy scale is provided by $k_B T$. On a physical basis, all these VACF data show well-known features such as an evident first negative minimum (the "cage effect," present in all fluids at high densities) followed by less pronounced oscillations. The latter (absent in Lennard-Jones liquids) are due to the more symmetrical shape of the main potential well of $v(r)$ in liquid metals.

As already pointed out, these data also provide an accurate quantitative test for the modern theories of liquid dynamics. The quantity of direct theoretical interest for the VACF is the memory function $K(t)$, connected to the normalized VACF $\psi(t)$ by the simple memory equation

$$\psi(z) = [z + K(z)]^{-1} , \tag{1}$$

where $\psi(z)$ and $K(z)$ are the respective Laplace transforms of $\psi(t)$ and $K(t)$. Broadly speaking, $K(t)$ has a fast initial decay with a typical time scale of some 10^{-14} s: this rapid decrease becomes instantaneous for hard spheres, due to the effect of binary collisions. In a system with a continuous $v(r)$, the initial decay of $K(t)$ can approximately be characterized by a single time constant τ_B, of the order of the duration of a "binary" collision. In particular, the assumption that this mechanism is the only decay channel for $K(t)$ implies a diffusion coefficient given by

$$D = (k_B T / M) \left[\int_0^\infty dt \, K(t) \right]^{-1}$$
$$\approx c \, (k_B T / M \Omega_0^2 \tau_B) \equiv D_B , \tag{2}$$

where c is a constant of the order unity, and Ω_0^2 (the square of the so-called Einstein frequency) is the initial value of $K(t)$. Both Ω_0^2 and τ_B are directly evaluable from $v(r)$ and purely structural data.

The binary result (2) is appealingly simple, but unfortunately in the liquid range D_B turns out to overestimate the actual diffusion coefficients by as much as 50%. As a matter of fact, the previous theory misses another important decay mechanism which yields a considerably slower decrease of $K(t)$ at intermediate and long times. Mode-coupling (MC) approaches are the natural tool to extract these long-lasting features; for the VACF the general framework has been established some time ago [8], and it has recently been made of much simpler applicability by the use of well-defined physical approximations [9]. As a result of these approaches, the full memory function can be split as $K(t) = K_B(t) + K_{MC}(t)$, where $K_B(t)$ is the binary contribution and $K_{MC}(t)$ the mode-coupling "tail." Although $K_{MC}(t)$ is nearly negligible at short times, its long-lasting nature has important effects both on the dynamics of the VACF and on the diffusion coefficient. In the liquid range, this slowly varying character is found [9] to be due to the coupling of single-particle variables to the density fluctuations with wave vector $k \approx k_m$, namely those with a pronounced "de Gennes" slowing down. This circumstance yields a considerable simplification in the analysis of MC decay chan-
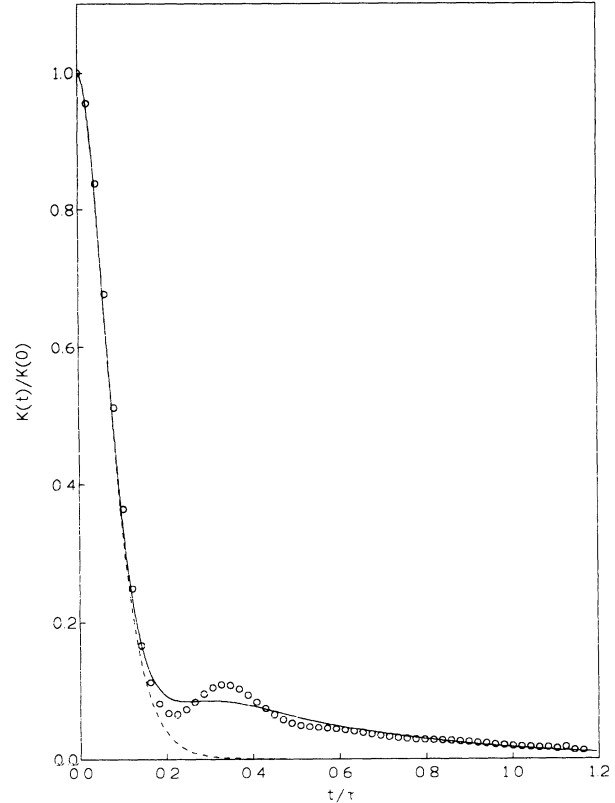

FIG. 5. The scaled memory function $K(t)$ of the velocity autocorrelation function (solid line: complete theory; dashed line: binary contribution). The open circles are our scaled simulation data for Na, K, Rb, and Cs. The differences among the systems are not appreciable.

nels (see Ref.[9] for a detailed derivation). The memory function evaluated in such a way and properly scaled is compared in Fig. 5 with the $K(t)$ obtained from the VACF simulation data. Even if there are some discrepancies around $t/\tau \approx 0.35$ (where the theory predicts a shoulder rather than the broad peak of the computer data), the important dynamical features of $K(t)$ appear to be satisfactorily reproduced. In particular, the full theory accounts quantitatively for the appearance of two distinct time scales in $K(t)$, thus improving substantially the results of the binary approach.

TABLE I. Diffusion coefficients (in units 10^{-5} cm^2/s) in several liquid alkali metals near the melting point. D_B and D are the values predicted by the binary and the full theories, respectively, D_{CS} is our simulation finding, and D_{expt} is the value observed in real experiments at melting as reported in Ref. [10].

	D_B	D	D_{CS}	D_{expt}
Na	6.30	4.11	4.06	4.06–4.35
K	5.66	3.61	3.58	3.52–3.72
Rb	3.89	2.46	2.40	2.60
Cs	3.33	2.13	2.11	2.16

Since the theory is able to reproduce the main dynamical details of the VACF memory function, an equally good agreement is expected for the diffusion coefficient which is inversely proportional to the area under $K(t)$. Table I shows that this is indeed the case. The satisfactory comparison among the theoretical results for D, our MD simulation findings, and the data from real experiments for all the liquid metals can be viewed as a sort of summary of all the main points addressed in the present work.

[1] J. R. D. Copley and J. M. Rowe, Phys. Rev. A **9**, 1656 (1974).

[2] T. Bodensteiner, C. Morkel, P. Müller, and W. Gläser, J. Non-Cryst. Solids **117-118**, 941 (1990); C. Morkel and T. Bodensteiner, J. Phys. Condens. Matter **2**, SA251 (1990).

[3] R. D. Mountain, in *Proceedings of the Third International Conference on Liquid Metals, Bristol, U.K., 1976*, edited by R. Evans and D. A. Greenwood, IOP Conf. Proc. No. 30 (Institute of Physics and Physical Society, London, 1977), p. 62; M. J. Huijben and W. van der Lugt, Acta Cryst. A **35**, 431 (1979); N. Matsuda, H. Mori, K. Hoshino, and M. Watabe, J. Phys. Condens. Matter **3**, 827 (1991).

[4] W. van der Lugt and B. P. Alblas, in *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell Scientific, Oxford, 1985), p. 299.

[5] D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B **2**, 2983 (1970).

[6] A. Rahman, Phys. Rev. A **9**, 1667 (1974).

[7] U. Balucani, A. Torcini, and R. Vallauri (unpublished).

[8] L. Sjögren and A. Sjölander, J. Phys. C **12**, 4369 (1979); L. Sjögren, J. Phys. C **13**, 705 (1980).

[9] U. Balucani, R. Vallauri, T. Gaskell, and S. F. Duffy, J. Phys. Condens. Matter **2**, 5015 (1990).

[10] M. Gerl and A. Bruson, see Ref. [4], p. 843.