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Molecular-dynamics study of the dynamic properties of fcc transition and simple metals in the liquid phase using the second-moment approximation to the tight-binding method

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Using a semiempirical many-body potential based on the second-moment approximation to the tight-binding method, we performed molecular-dynamics simulations to compute the diffusion constants and shear viscosities of the fcc transition metals Ni, Pd, Pt, Cu, Ag, and Au and the simple fcc metals Al and Pb in the liquid phase; in the case of Ni and Pb, we also computed the dynamic structure factors. Comparison of the molecular-dynamics results with available experimental data shows that the tight-binding potentials give a reasonable description of the dynamic properties of the liquid metals considered, in spite of having been parametrized on the basis of solid-state data. [S0163-1829(99)09937-3]

Many-body semiempirical potentials, such as those based on the embedded atom model (EAM) (Ref. 1) or the tight-binding method (TBM),[2] were developed to overcome the limitations of the pair-potential approach for describing metallic bonding, and have been widely used to compute the energies of metallic systems for computer simulation purposes (see, e.g, Refs. 3, 4, and those cited therein). One of the simplest semiempirical potentials derives from the second-moment approximation to the TBM (TBM-SMA).[5] In this TBM-SMA potential, which has successfully been used to analyze bulk and surface properties of transition metals and alloys[4,6,7] and to study mesoscale systems such as clusters of metal atoms (see, e.g., Ref. 8), the cohesive energy of the system is the sum of an effective band term (in which many-body effects are included) and a short-range repulsive pair potential. Although the governing equation of the TBM-SMA is formally equivalent to that of the EAM, the physical rationales of these two methods are quite different.

One of the main issues in the evaluation of semiempirical many-body potentials is the transferability of their parameters, i.e., their applicability to systems differing from those used to obtain the parameters of the potential. Generally, the potential parameters are derived from one-temperature solid-state properties, so that a major question is whether the same potential is able to describe the behavior of the liquid phase, with its quite different electron densities and interatomic separation distributions. Since the pioneering work of Foiles,[9] several studies have analyzed the ability of the EAM to describe the static structure and thermodynamic and dynamic properties of liquid transition metals (see, e.g., Ref. 10 and those cited therein). The TBM-SMA, however, has received less attention in this area: as far as we know, the only extensive applications of the TBM-SMA to liquid metals have been carried out by Cleri and Rosato,[4] Gómez *et al.*[6] and Liu *et al.*[7] These studies analyzed the static properties of liquid transition metals and of some liquid simple metals such as Al and Pb, but not transport coefficients such as the diffusion constant D or the shear viscosity η, which are related to single-particle and collective dynamic properties, respectively.[11] Even allowing for the greater computational demands of dynamic properties, this is somewhat surprising, since for the purposes of molecular-dynamics (MD) simulations the TBM-SMA has the advantage over the EAM that it gives an explicit expression for the band energy,[4,5] whereas the embedding function of the standard EAM (which represents the energy required to embed each atom in the local electron density created by the remaining atoms) must be constructed numerically once the pairwise potential and the electron density are known.[12,13]

In the work described here we investigated the ability of the TBM-SMA to describe the dynamic properties of liquid metals by performing MD simulations to compute D and η for the fcc transition metals Ni, Pd, Pt, Cu, Ag, and Au and the simple fcc metals Al and Pb, comparing the results with experimental data wherever possible.[14] For Ni and Pb we also computed, and compared with available data,[15,16] the dynamic structure factor $S(q,\omega)$. For each metal studied, the TBM-SMA parameters used were those obtained by Cleri and Rosato[4] from a fit to the experimental values of the cohesive energy, atomic volume, and elastic constants of the crystal at $T=0$ K. Since the TBM-SMA is described in detail in Refs. 4 and 5, it will not be explained here. In what follows we sketch the computational method employed in our calculations, present and discuss our results, and summarize our main conclusions.

We studied all the metals considered in states near their melting points characterized by the temperatures T and atomic number densities ρ listed in Table I (liquid densities were taken from Ref. 17); in the case of Ni, calculations were also performed at $T=1875$ K, $\rho=0.078$ Å^{-3}, so as to compare computed $S(q,\omega)$ values with available experimental data at that temperature.[15] Using the TBM-SMA expression for the energy of each metal (which includes interactions out to the fifth-neighbor distance[4]), we performed MD simulations for a system of $N=500$ atoms in a cubic box with periodic boundary conditions. The computational procedure was as follows. First, we melted an fcc structure to obtain an initial configuration (i.e., the positions and velocities of the particles) at the chosen density ρ and temperature T, and performed a canonical MD simulation using the Nosé

TABLE I. Values of the diffusion constants D and shear viscosities η of the liquid metals studied, as computed using the Green-Kubo (GK) and Einstein (E) relations at the temperatures and atomic number densities specified, and available experimental data (Ref. 14).

	T (K)	ρ (Å^{-3})	D(Å^2 ps^{-1})			η (eV ps Å^{-3})		
			GK	E	Expt.	GK	E	Expt.
Ni	1775	0.0792	0.252 ± 0.004	0.254 ± 0.004		0.036 ± 0.005	0.037 ± 0.006	0.0311
Pd	1853	0.0594	0.403 ± 0.003	0.407 ± 0.003		0.023 ± 0.003	0.023 ± 0.003	
Pt	2053	0.0577	0.281 ± 0.003	0.285 ± 0.003		0.038 ± 0.006	0.039 ± 0.006	
Cu	1423	0.0755	0.272 ± 0.003	0.276 ± 0.003	0.471	0.027 ± 0.003	0.027 ± 0.003	0.0248
Ag	1273	0.0517	0.265 ± 0.004	0.270 ± 0.004	0.281	0.023 ± 0.002	0.023 ± 0.002	0.0230
Au	1423	0.0525	0.260 ± 0.003	0.264 ± 0.002		0.025 ± 0.003	0.024 ± 0.003	0.0271
Al	943	0.0528	0.468 ± 0.006	0.470 ± 0.006		0.010 ± 0.003	0.010 ± 0.003	0.0077
Pb	613	0.0310	0.133 ± 0.003	0.134 ± 0.003	0.183	0.020 ± 0.003	0.020 ± 0.003	0.0157

constant-temperature technique;[18] the equations of motion were solved using a fourth-order Gear predictor-corrector algorithm[18] with a time step of 10^{-4} ps. The energy of the system was calculated by averaging over 10^4 time steps after an appropriate initial period for equilibration. Then, starting from a configuration with an energy very close to the average value so obtained, microcanonical MD simulations were performed using the velocity Verlet algorithm[18] with a time step of 2×10^{-3} ps. After an appropriate initial equilibration period, a configuration was recorded every 0.01 ps (5 time steps). In order to be able to estimate the statistical uncertainty of the results of these microcanonical simulations, the properties of interest were averaged within each of twelve successive runs of 25×10^3 time steps (i.e., over the 5×10^3 configurations recorded in every run). It is worth noting that the pressures obtained in our simulations, 6–70 kbar, were small compared with the bulk moduli of the metals simulated, which are of the order of 1 Mbar.[19] This indicates that the equilibrium zero-pressure densities will be very close to the experimental values.

For each liquid metal considered, the diffusion constant D was calculated from the mean-square displacement using Einstein's formula and from the velocity autocorrelation function using the Green-Kubo relation.[11,18] Similarly, the shear viscosity was computed using the Green-Kubo and generalized Einstein formulas.[11,18] In the cases of Ni and Pb we also computed their dynamic structure factors $S(q,\omega)$ as the Fourier transforms of the corresponding intermediate scattering functions $F(q,t)$.[11]

Although our primary objective in this study was to investigate the dynamical properties of the liquid metals, we also computed their static structure factors $S(q)=F(q,0)$ (Ref. 11) so as to allow comparison with available experimental data.[16,17] Figure 1 shows that, in general, there is good agreement between the computed $S(q)$ values for the states listed in Table I and Waseda's x-ray results.[17] The main discrepancies occur for Ni and Pb, notably in the heights of the main $S(q)$ peaks. As has been pointed out in other theoretical studies of the properties of liquid metals (see, e.g., Ref. 10), the method used by Waseda to analyze his x-ray measurements may underestimate the main $S(q)$ peak somewhat. In the case of Pb, our $S(q)$ results are in much better agreement with neutron-scattering data reported by Söderström for $T=623$ K.[16]

In Table I we compare the computed values of D and η with the available experimental data.[14] We first note that the

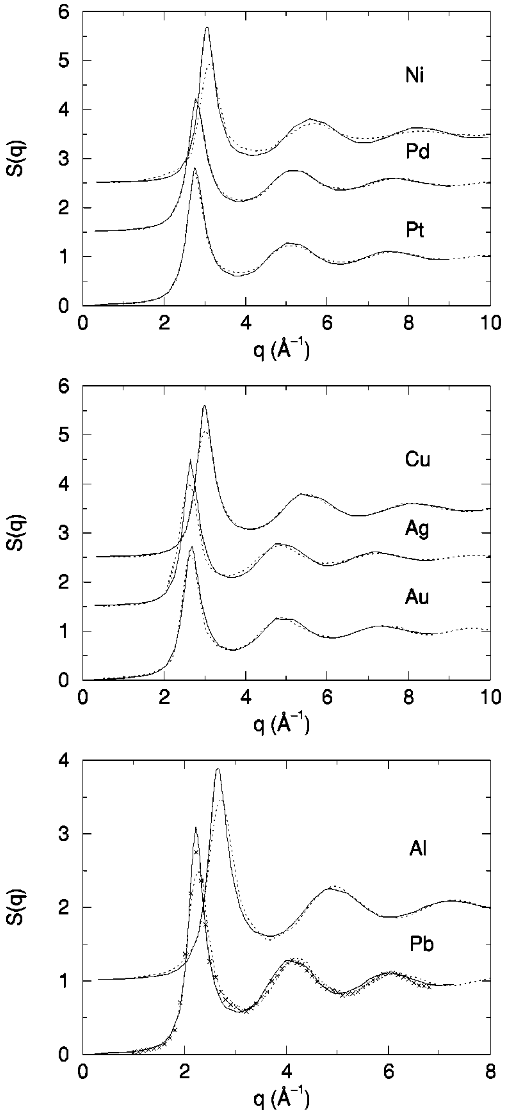

FIG. 1. Comparison of the static structure factors of liquid Ni, Pd, Pt, Cu, Ag, Au, Al, and Pb, as calculated using the TBM-SMA potential in the states listed in Table I (solid curves), and as obtained by Waseda from x-ray data (Ref. 17) (dashed curves). In the case of Pb, neutron-scattering results obtained by Söderström (Ref. 16) at $T=623$ K are also shown (crosses). The y coordinates are correct for the Pt, Au, and Pb curves; the Al curve is shifted up by 1, the Pd and Ag curves by 1.5, and the Ni and Cu curves by 2.5.

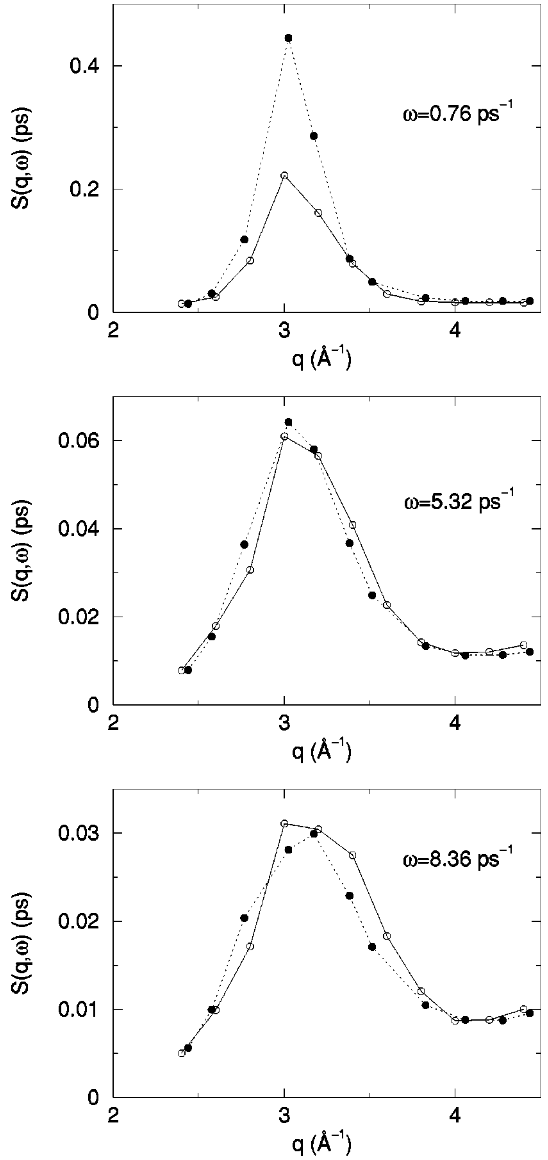

FIG. 2. Comparison of the computed dynamic structure factor of liquid Ni at $T=1875$ K, $\rho=0.078$ Å^{-3} for several values of ω (solid circles) with the experimental data reported by Johnson *et al.* (Ref. 15) at $T=1870\pm10$ K (open circles). Lines joining points are merely visual aids.

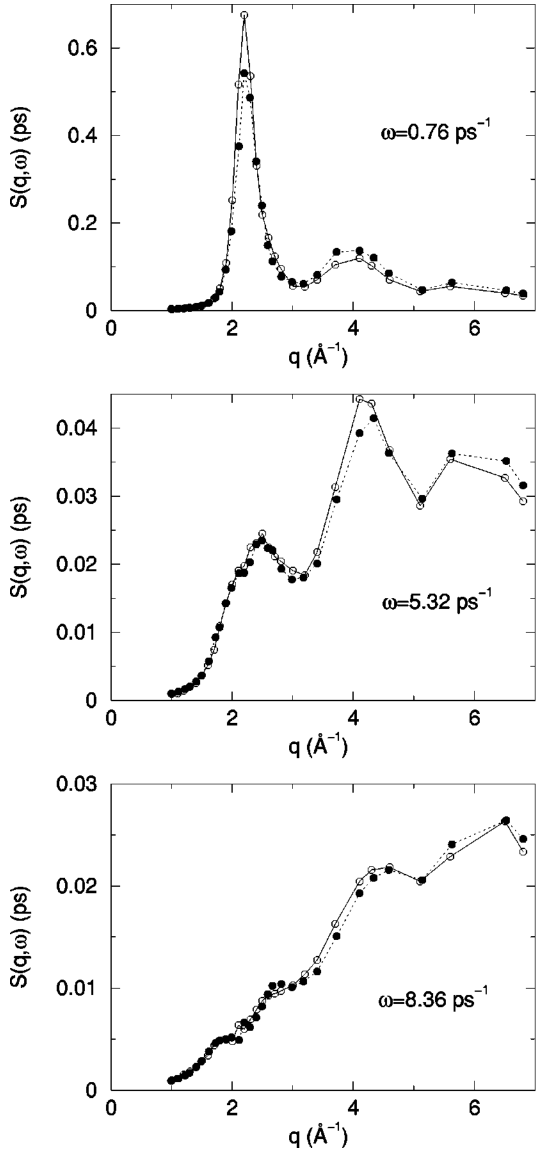

FIG. 3. Comparison of the computed dynamic structure factor of liquid Pb at $T=613$ K, $\rho=0.0310$ Å^{-3} for several values of ω (solid circles) with the experimental data reported by Söderström (Ref. 16) at $T=623$ K (open circles). Lines joining points are merely visual aids.

values of D and η computed using the Green-Kubo and Einstein relations are mutually consistent. For the metals for which experimental data for the shear viscosity η are available (all except Pd and Pt), our computed values of this transport coefficient are in very good agreement with the experimental results. Of the metals studied here, the only ones for which the diffusion constant D has been measured are Cu, Ag, and Pb. For Ag, our calculated values agree very well with the experimental data, and the agreement is also quite good with one of the published experimental values for Pb [the value for Pb shown in Table I was preceded by the value 0.237 Å^2 ps^{-1} at 613 K (Ref. 14)]. However, our MD results for Cu differ considerably from the experimental value reported in Ref. 14.

In principle, this discrepancy for Cu might be suspected of indicating inadequate parametrization of the TBM-SMA potential for liquid Cu. However, as pointed out in Ref. 20, there are reasons to believe that the reported experimental value of D for this liquid metal may be in error. The diffusion constant and the shear viscosity are connected through the Stokes-Einstein relation, $D\eta=kT/(2\pi a)$, where k is the Boltzmann constant and a is the diameter of the diffusing particles;[11] though exact only for the Brownian motion of a macroscopic particle, this relation can also be used to estimate atomic diffusion constants in liquids. If this is done for Cu, Ag, and Pb using the experimental shear viscosities and particle radii deduced from the atomic densities, the value obtained for Cu, 0.268 Å^2 ps^{-1}, differs much more widely from the reported experimental data than do the values obtained for Ag and Pb, 0.228 Å^2 ps^{-1} and 0.136 Å^2 ps^{-1}, respectively. This argument, though simple, suggests that the experimental value of D for liquid Cu at $T=1423$ K reported in Ref. 14 is indeed probably overestimated. Furthermore, the values of D obtained for liquid Cu in this paper are in keeping with the *ab initio* MD result of Pasquarello *et al.*,[21] 0.28 ± 0.02 Å^2 ps^{-1}.

Our TBM-SMA values of D and η for liquid Al are consistent with the values recently otained by *ab initio* MD calculations, 0.68 Å^2 ps^{-1} and 0.0087 eV ps Å^{-3} (Ref. 22), given that the latter were calculated for $T=1000$ K. Our values for the fcc transition metals Ni, Pd, Pt, Cu, Ag, and Au are generally in good agreement with the values previously computed,[10,20] for the same thermodynamic states, using the Voter and Chen (VC) version of the EAM.[13] The most significant difference concerns the diffusion constant of liquid Ni: the VC EAM values obtained using the Green-Kubo and Einstein relations were, respectively, 0.352 ± 0.005 and 0.356 ± 0.004 Å^2 ps^{-1} (Ref. 10), which are somewhat higher than the TBM-SMA values listed in Table I. As indicated above, there are no experimental values of the diffusion constant of liquid Ni with which to compare calculated values, but there are reasons to believe that the VC EAM results are more accurate than those obtained using the TBM-SMA: we have recently shown[10,23] that the VC EAM gives a good description of the static structure and thermodynamic properties of liquid Ni even at high temperatures, whereas the TBM-SMA description of these properties is less accurate,[4,7] at least when, as in the present paper, the parameters obtained by Cleri and Rosato[4] are used.

In Figs. 2 and 3 we compare, for liquid Ni at $T=1875$ K, $\rho=0.078$ Å^{-3} and liquid Pb at $T=613$ K, $\rho=0.0310$ Å^{-3}, the dynamic structure factor $S(q,\omega)$ at $\omega=0.76$, 5.32, and 8.36 ps^{-1} as determined from our TBM-SMA MD simulations and from neutron-scattering data.[15,16] In general, the agreement between the computed values of $S(q,\omega)$ and the experimental data is very good. The only significant discrepancies occur for liquid Ni at the lowest frequency and wave numbers close to 3.03 Å^{-1}, the position of the main peak of the MD static structure factor of Ni at $T=1875$ K; like the similar discrepancies found in our earlier VC EAM-based MD study of liquid Ni,[10] they are probably mainly due to errors in Johnson *et al.*'s work-up of their experimental data in the region near $\omega=0$, rather than to inadequacy of the semiempirical potential used.

To sum up, the TBM-SMA potential, even when parametrized solely on the basis of solid-state data, is capable of providing a reasonably good description of the dynamic properties of the fcc metals Ni, Pd, Pt, Cu, Ag, Au, Al, and Pb in the liquid phase. This result is not obvious *a priori*, since there are potential models for transition metals that give a good description of the solid state but a very poor approximation for the static structure factor of the liquid phase (see, e.g., Refs. 9 and 24). For the metals studied here for which no experimental values of D or η are yet available, the computed values listed in Table I may, with the probable exception of the diffusion constant of liquid Ni, prove useful to researchers who need these data. Similarly, the results of Figs. 2 and 3 show that the TBM-SMA potential may be useful for describing the dynamic structure factors and other collective dynamic properties of transition and simple liquid metals, the experimental determination of which may be difficult or, as in the case of the transverse current correlation function,[11] impossible. These considerations seem likely to be valid not only for the fcc metals discussed here, but also for hcp transition metals, for which TBM-SMA potential parameters have also been obtained from solid-state data.[4]

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