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Kohn-Sham *ab initio* molecular dynamics study of liquid Al near melting

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A comprehensive study of static, dynamic and electronic properties of liquid Al in a thermodynamic state near its triple point was performed by means of 205-particle *ab initio* molecular dynamics simulations using Kohn-Sham density-functional theory and the Langevin equation of motion. The good agreement of the results with experimental findings shows that the use of this technique to achieve a reliable description of the behavior of liquid metals, including their dynamic properties, is not beyond current computational capacities, at least in the case of simple liquid metals such as Al.

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I. INTRODUCTION

Molecular dynamics (MD) is a powerful simulation technique for the study of condensed matter. In classical molecular dynamics (CMD) the simulated particles are moved in accordance with the dictates of between-particle potentials, electronic degrees of freedom remaining hidden. By contrast, in *ab initio* MD (AIMD) methods, the forces on the nuclei are computed using electronic structure calculations that are performed as the MD trajectory is generated. In particular, recent years have seen a marked increase in the use of AIMD methods based on density-functional theory (DFT),[1,2] which for given nuclear positions apply the Hellmann-Feynman theorem to obtain the forces acting on the nuclei following calculation of the ground-state density and energy of the valence electrons. In DFT-based AIMD simulations, the nuclear positions thus evolve in accordance with classical mechanics while the valence electron subsystem follows adiabatically.

The computational demands of DFT-based AIMD methods using the Kohn-Sham approach (KS-AIMD methods) grow very rapidly with the size of the system studied, which has limited both system size itself and the duration of the simulated evolution of the system. As a result, although several hundred papers have reported KS-AIMD studies of liquid systems, we know of only four that have attempted to calculate dynamical properties other than the self-diffusion coefficient [two reporting results on the dynamical structure factors of Li (Ref. 3) and Ge (Ref. 4), and two results on the autocorrelation functions of the stress tensors of Al, Se, Fe, and FeS (Refs. 5 and 6)], and of these four at least one appears to have bitten off rather more than it could chew [the study of Li (Ref. 3) overestimated the dynamic structure factor more than 100-fold for small wave vectors]. Even calculations of static properties of liquid metals can differ significantly from experimental results if too few atoms are simulated.[7]

Less restrictive computational demands are made by the orbital-free DFT approach (OF-AIMD), which by using an approximate expression for the electronic kinetic energy functional avoids the need to calculate orbitals and hence succeeds in greatly reducing the number of variables describing the electronic state, thereby allowing simulation of the evolution of larger systems (up to several hundred particles) over longer times (several tens of ps). However, although OF-AIMD has achieved good estimates of both static and dynamic properties for some simple liquid metals and binary alloys,[8,9] the accuracy of its results for more complex systems is likely to be limited by its using an approximate electronic kinetic energy functional and a local pseudopotential. Moreover, its ignoring orbitals means that it cannot be used to calculate certain electronic properties (notably density of states, conductivities and optical properties). It is accordingly of interest to continue to explore the applicability of KS-AIMD methods, lest they be shunned even when their computational demands are not, in fact, excessive.

Liquid Al may be considered as a simple metal in which the core electrons are clearly distinct from the valence electrons and do not significantly overlap those of neighboring ions. Its static structure factor has been measured experimentally using both neutron[10] and x-ray[11,12] diffraction, and its dynamic structure near the triple point has been investigated[13] by inelastic x-ray scattering (IXS) in the wave number region $0.05q_p \leqslant q \leqslant 0.5q_p$, where q_p (≈ 2.70 Å^{-1}) is the position of the main peak of the static structure factor. Most simulation studies of liquid Al have treated it as a collection of ions interacting through density-dependent effective interionic pair potentials derived from ionic pseudopotentials by application of linear response theory and second-order perturbation theory. However, CMD simulations of this kind have given results that fail to agree with the experimental data for the static structure factor[14,15] or the dynamic structure factor.[16] OF-AIMD calculations, on the other hand, have achieved reasonable agreement with experiment for both static and dynamic properties.[8,17]

KS-AIMD has previously been used to study the static structure,[18,19] self-diffusion coefficient,[5,6,19] shear viscosity coefficient[5,6] and electronic properties[18] of liquid Al. Silvestrelli's[18] calculations of the static structure and electronic properties for several thermodynamic states with temperatures in the range 1000–8000 K, which used 72 particles and simulated times of ≈1 ps, predicted a typically metallic electronic density of states and afforded a calculated conductivity in quite good agreement with experiment.[20] Bloch and Parrinello[19] used 64 particles and a non-local Bachelet-Hamann-Schlüter pseudopotential[21] in their calculations of the static structure and self-diffusion coefficient near the triple point. Gillan and co-workers[5,6] calculated the self-diffusion and shear viscosity coefficients using 64 particles and the ultrasoft Vanderbilt pseudopotentials of VASP.[22]

Here we describe a comprehensive 205-particle KS-AIMD study of static, dynamic and electronic properties of liquid Al near its triple point. In Sec. II we briefly describe the theory and implementation of the KS-AIMD method used (for further details see Refs. 23); in Sec. III we present and discuss our results, comparing them with experimental data and with those of other simulation studies; and in Sec. IV we summarize our main conclusions.

II. COMPUTATIONAL METHOD

According to DFT,[1,2] the total energy E_{tot} of a system comprising electrons and ions (the latter in positions $\{\mathbf{R}_a\}$) can be written as a unique functional of the electron density ρ:

$$E_{\mathrm{tot}}[\rho] = T_s[\rho] + E_{\mathrm{ion}}(\{\mathbf{R}_a\},[\rho]) + E_H[\rho] + E_{\mathrm{xc}}[\rho] + E_{\text{ion-ion}}(\{\mathbf{R}_a\}), \tag{1}$$

where $T_s[\rho]$ is the kinetic energy of a system of noninteracting electrons with density ρ, $E_{\mathrm{ion}}(\{\mathbf{R}_a\},[\rho])$ is the electron-ion energy, $E_H[\rho]$ is the electron-electron Coulomb energy or Hartree potential energy, $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation energy, and $E_{\text{ion-ion}}(\{\mathbf{R}_a\})$ is the classical electrostatic energy among the ions. Minimization of this expression by variation of the function ρ provides the ground-state energy of the system, and the density that yields this minimum value is the exact ground-state density.

In this work, $E_{\mathrm{xc}}[\rho]$ was calculated using the local density approximation (LDA) as parameterized by Perdew and Zunger.[24] $E_{\mathrm{ion}}(\{\mathbf{R}_a\},[\rho])$ was constructed using norm-conserving nonrelativistic s, p, and d pseudopotentials[25] generated for the reference ground-state configuration [Ne] $3s^2 3p^1 3d^0$ with radial cutoffs of 2.6 a.u., and was made separable[26] using the d pseudopotential as the local potential. In performing the simulation, we did not resort to fictitious electronic dynamics, as in some other KS-AIMD methods,[27,28] but recomputed the Kohn-Sham orbitals for each ion configuration,[23] thereby keeping the system on the Born-Oppenheimer surface. This procedure has in previous work allowed calculation of structural and electronic properties of the liquid semiconductor systems Si, Ge, GaAs, CdTe, and GeTe.[29]

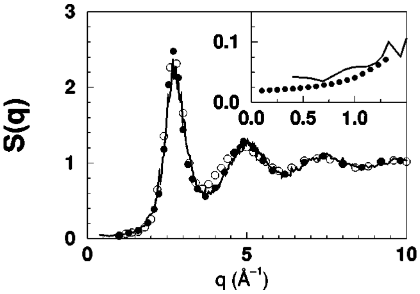

FIG. 1. Static structure factor of liquid Al at 1000 K. Solid dots: x-ray diffraction data (Refs. 11 and 12). Circles: neutron diffraction data (Ref. 10). Continuous line: present *ab initio* simulations.

Calculations were performed for a thermodynamic state characterized by the number density $\rho_n = 0.0529$ Å^{-3} and the temperature $T = 1000$ K (70 K above the melting point). 205 atoms were placed at random in a cubic supercell; the cell was coupled to a virtual heat bath via the Langevin equation of motion[23] and was heated to far above the target temperature in order to eradicate any memory of its initial configuration; the system was then jumped to 1000 K, allowed to stabilize, and gradually decoupled from the virtual heat bath; and finally a microcanonical KS-AIMD simulation was performed over 850 time steps (5.1 ps of simulated time), ion dynamics being generated using the Beeman algorithm[30] with Hellmann-Feynman forces. Throughout, a plane-wave representation with an energy cutoff of 12 Ry was used, and the Brillouin zone was sampled at the single Γ point. During the microcanonical simulation, the rms deviation from conservation of energy was $\approx 4 \times 10^{-5}$ eV/atom and the drift rate for the total energy was $\approx 0.006 \times 10^{-5}$ eV/atom per ps. The rms fluctuation in temperature was ≈100 K; the average temperature was 1010 K (only 1% greater than the temperature set through the Langevin equation); and the average pressure was 1.7 GPa. We estimate that average pressure would have been zero using a cell with a volume about 2.5% smaller; the negative value actually observed is mainly attributable to the LDA, which is wont to underestimate equilibrium volumes. Only data from the microcanonical simulation were used in calculating the static, dynamic, and electronic properties reported below.

III. RESULTS AND DISCUSSION

A. Static properties

Discrepancies among the results for the static structure factor $S(q)$ obtained in this work, by x-ray experiments at 1023 K and $\rho_n = 0.0525$ Å^{-3},[11,12] and by neutron diffraction experiments at 943 K and $\rho_n = 0.0530$ Å^{-3},[10] mainly affect the region 3.5 Å$^{-1} \leqslant q \leqslant 5.0$ Å^{-1}, where the present results agree well with the x-ray data but the neutron values are slightly higher (Fig. 1). Fairly good agreement between the computed and x-ray values continues into the low-q region (Fig. 1, inset).

As in other simple liquid metals near melting,[31] local geometry appears to be quasi-icosahedral: integration of the computed pair distribution function $g(r)$ up to its first mini-

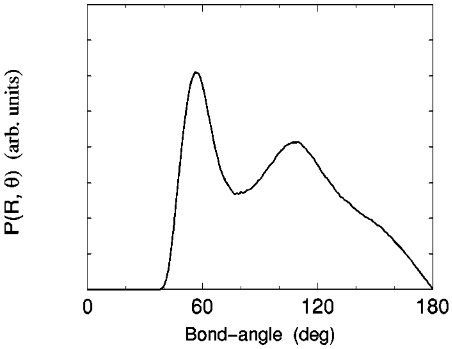

FIG. 2. Calculated bond angle distribution function $P(R_{\min},\theta)$ for liquid Al at 1000 K.

mum, $R_{\min}$, gives a coordination number $N_c=11.4$, and the distribution of bond angles defined by atoms up to $R_{\min}$ away peaks near 56° and 110° (Fig. 2).

B. Dynamic properties

1. Single particle dynamics

The normalized velocity autocorrelation function $Z(t)$, calculated as

$$Z(t)=\frac{\langle \mathbf{v}_a(t)\cdot\mathbf{v}_a(0)\rangle}{\langle \mathbf{v}_a(0)\cdot\mathbf{v}_a(0)\rangle}, \tag{2}$$

where $\mathbf{v}_a(t)$ is the velocity of ion a and angle-brackets indicate an ensemble average, exhibits the backscattering and other features typical of simple metals near melting (Fig. 3).[31–33] Its first minimum has a depth of about 0.12, and the following maximum is rather weak, with a value close to zero. Recent OF-AIMD simulations[8] for 943 and 1323 K obtained similar functions, although the first minimum for 943 K, the temperature nearest that considered in the present work, is rather deeper than in this work (Fig. 3).

The self-diffusion coefficient D was found to be $0.65\ \text{Å}^2/\text{ps}$ when calculated as the time integral of $Z(t)$, and $0.70\ \text{Å}^2/\text{ps}$ when calculated as the slope of the mean square ion displacement function $\Delta R^2(t)\equiv\langle|\mathbf{R}_a(t)-\mathbf{R}_a(0)|^2\rangle$. No experimental data for this parameter are available, but the OF-AIMD calculations mentioned above afforded an interpolated value of $0.60\pm0.05\ \text{Å}^2/\text{ps}$ for $T=1000$ K.[8] The previous KS-AIMD simulations mentioned in the Introduction gave values of $0.60\ \text{Å}^2/\text{ps}$ [calculated as the slope of $\Delta R^2(t)$] for a thermodynamic state near the triple point,[19] and $0.52-0.68\ \text{Å}^2/\text{ps}$ for $T=1000$ K.[5]

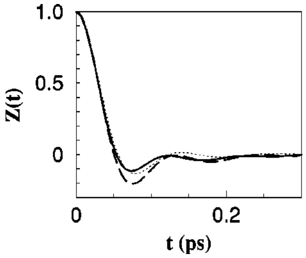

FIG. 3. Normalized velocity autocorrelation function of liquid Al at 1000 K. Continuous line: present *ab initio* simulations. Dashed and dotted lines: OF-AIMD results for $T=943$ and 1323 K, respectively (Ref. 8).

2. Collective dynamics

The collective dynamics of density fluctuations in liquids are usually described by means of the intermediate scattering function,

$$F(q,t)=\frac{1}{N}\left\langle\sum_{l,m}\exp\{-i\mathbf{q}\cdot[\mathbf{R}_l(t)-\mathbf{R}_m(0)]\}\right\rangle \tag{3}$$

(where N is the total number of atoms), and by its Fourier transform with respect to time, the dynamic structure factor $S(q,\omega)$, which is directly related to the intensity of scattering in inelastic neutron or x-ray scattering experiments. For homogeneous isotropic systems, the $\mathbf{q}$-dependence of $F(q,t)$ and $S(q,\omega)$ reduces to dependence on the modulus $q=|\mathbf{q}|$.

Like both CMD (Ref. 16) and OF-AIMD (Ref. 8) calculations, the present study found $F(q,t)$ to exhibit damped oscillations with respect to t, the damping increasing with q, so that for q greater than about half q_p the decay was monotonic. For $q\leqslant0.5\ \text{Å}^{-1}$, $F(q,t)$ was still significantly nonzero at the end of the simulated time, making calculation of its Fourier transform with respect to time meaningless, but for larger wave numbers $S(q,\omega)$ was calculated, cutoff noise being minimized (at the cost of a slight broadening and lowering of spectral side peaks) by means of a window function enforcing roll-off to zero as the end of the simulated time was approached. Overall, the results agree somewhat better with IXS data[13] than do those of the OF-AIMD simulations[8] mentioned above, in spite of the latter having used 500 particles and 30 ps of simulated time (Fig. 4); in particular, the side peaks present in these spectra up to $\approx1.5\ \text{Å}^{-1}$, which reflect collective density excitations, are clearly exaggerated by OF-AIMD, although both techniques err in locating these side peaks at smaller wave numbers than the experimental results. Spectra rather similar to the OF-AIMD spectra were obtained by taking the Fourier transform of the result of fitting the calculated $F(q,t)$ with an eight-parameter analytical expression that interpolates among the ideal gas, viscoelastic and hydrodynamic models.[16]

As far as we know, there have only been two previous attempts to calculate the dynamic structure factor of a liquid metal by KS-AIMD: Kresse's 128-atom study of Li near melting,[3] and Chai *et al.*'s 64-atom study of Ge,[4] both of which used VASP (Ref. 22) with an ultrasoft pseudopotential. Kresse's results grossly overestimated $S(q,\omega)$ for small q [e.g., by factors of 30 and 100 for $S(q,0)$ at $q=1.25$ and $0.72\ \text{Å}^{-1}$, respectively], while Chai *et al.* achieved agreement with experiment as regards the positions of side peaks but did not discuss their magnitudes. The fact that in the present study of Al the calculated side peak positions were close to those of 500-atom, 30 ps OF-AIMD simulations suggests that calculation of more accurate side peak positions may not necessarily require the use of numbers of atoms and/or simulated times that would be prohibitive for KS-AIMD, but may instead be achievable by less costly means such as modification of the ionic pseudopotential.

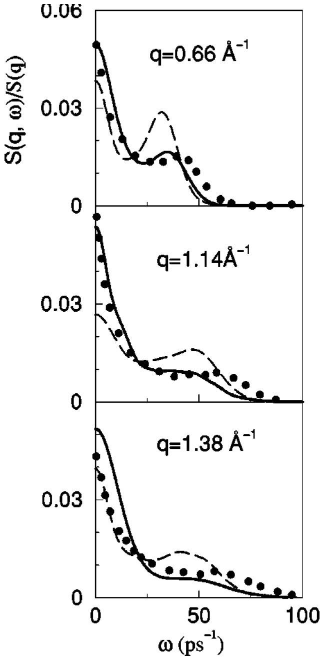

FIG. 4. Dynamic structure factor, $S(q,\omega)$, for several q values, for liquid Al at $T=1000$ K. Continuous line: present *ab initio* simulations. Dashed line: OF-AIMD simulations (Ref. 8). Solid dots: experimental data (Ref. 13).

The longitudinal and transverse current correlation functions are respectively defined by

$$C_L(q,t) = \langle j_L(q,t) j_L^*(q,0) \rangle \tag{4}$$

and

$$C_T(q,t) = \langle j_T(q,t) j_T^*(q,0) \rangle, \tag{5}$$

where $j_L(q,t)$ and $j_T(q,t)$ are the components of

$$\mathbf{j}(q,t) = \sum_a \mathbf{v}_a(t) \exp\,[i\mathbf{q}\cdot\mathbf{R}_a(t)], \tag{6}$$

that are respectively longitudinal and transverse to $\mathbf{q}$. Although in principle the Fourier transform of $C_L(q,t)$ with respect to time, $C_L(q,\omega)$, provides no more information than the dynamic structure factor, being identically equal to $\omega^2 S(q,\omega)$, the fact that $C_L(q,t)$ decays much faster than $F(q,t)$ makes it possible to perform the transform even for small q. Figure 5 shows plots of $\omega_L(q)$, the position of the peak of $C_L(q,\omega)$ for given q, as obtained in this work and by OF-AIMD,[8] together with the linear dependence predicted for small q by the experimental value of the adiabatic sound velocity $c_s \approx 4700$ m/s,[34] which is the slope of $\omega_L(q)$ in the limit $q\to 0$. The value of c_s predicted by fitting a straightline to the low-q $\omega_L(q)$ values obtained in this work, 4600 m/s, agrees reasonably well with the experimental value; the value given by OF-AIMD was 4850 m/s.[8]

The transverse current correlation function, $C_T(q,t)$, is not directly associated with any measurable quantity, but through computer simulations provides information on shear modes.

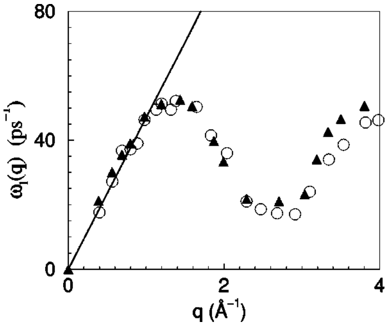

FIG. 5. Dispersion relation for liquid Al at 1000 K [$\omega_L(q)$ is the position of the peak of $C_L(q,\omega)$], as obtained in this work (open circles) and by OF-AIMD (full triangles; Ref. 8). Continuous line: linear dispersion predicted by the experimental hydrodynamic adiabatic sound velocity, $c_s = 4700$ m/s (Ref. 34).

In the free particle limit ($q\to\infty$) it is Gaussian with respect to both q and t, and in the hydrodynamic limit ($q\to 0$) is given by

$$C_T(q,t) = \frac{1}{\beta m} \exp\,(-q^2 \eta |t|/m\rho_n), \tag{7}$$

where η is the shear viscosity, m is the atomic mass and $\beta = (k_B T)^{-1}$ (k_B being the Boltzmann constant). In the present study the inelastic peak that appears at low q in its Fourier transform, $C_T(q,\omega)$, persisted up to $q\approx 3q_p$. The value of η obtained by extrapolating to $q=0$ the function

$$\tilde{\eta}(q,0) = \frac{\rho_n m}{q^2} \{[\beta m \tilde{C}_T(q,0)]^{-1} - z\}, \tag{8}$$

where $\beta m \tilde{C}_T(q,0)$ is the area under $C_T(q,t)$ following normalization [the memory function $\tilde{C}_T(q,z)$ being the Laplace transform of $C_T(q,t)$],[31,35,36] was 1.05 ± 0.15 GPa ps, close to the experimental value of 1.10 GPa ps obtained at $T = 990$ K.[37] The values given by previous KS-AIMD simulations,[5,6] which were calculated using the definition of η as the time integral of the autocorrelation function of the off-diagonal components of the stress tensor, were 1.4 GPa ps for $\rho_n = 0.0524$ Å^{-3} and 2.2 GPa ps for $\rho_n = 0.0551$ Å^{-3}.

The value of η afforded by the Stokes-Einstein relation[38] $\eta = K_B T/(2\pi d D)$ when D is set equal to 0.675 Å^2/ps (the average of the two values found in this work) and d to the position of the main peak of $g(r)$, 2.72 Å, is 1.19 GPa ps. The good agreement between this value and the value of 1.05 GPa ps calculated above supports the validity of using the Stokes-Einstein relation for atoms in this way. When the experimental values of η and d are substituted in the relation [the latter being given by the experimental[12] $g(r)$ as 2.78 Å], the resulting estimate of the self-diffusion constant for $T = 1000$ K is 0.71 Å^2/ps.

C. Electronic properties

Figure 6 shows the single-particle electronic density of states DOS(E) as calculated for the self-consistently com-

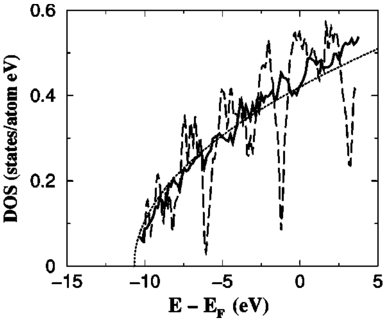

FIG. 6. Total electronic density of states for liquid Al at 1000 K. Continuous line: present results using four special points of the Brillouin zone. Dashed line: results using only the Γ point. Dotted line: free electron DOS.

puted Kohn-Sham eigenvalues by averaging over four special points **k** of the Brillouin zone and eight ionic configurations occurring over a period of 0.6 ps. In keeping with the results of Silvestrelli,[18] DOS(E) shows clearly metallic behavior, keeping quite close to the DOS curve for the free electron (in fact, the same is true when only the Γ point is sampled, except for some spurious minima).

As in KS-AIMD studies of other elements,[39] electrical conductivity, σ, was computed by extrapolating to $\omega=0$ the optical conductivity, $\sigma(\omega)$, calculated by averaging (over eight ionic configurations and four **k** points) the Kubo-Greenwood[40] formula

$$\sigma(\omega,\{\mathbf{R}_a\}) = \frac{2\pi e^2}{3m_e^2\Omega\omega}\sum_{i,j}(f_i - f_j)|\langle\psi_i|\hat{p}|\psi_j\rangle|^2\delta(E_j - E_i - \hbar\omega), \tag{9}$$

where e and m_e are the charge and mass of the electron, respectively, $\hat{p}$ is the momentum operator, and the ψ_i and E_i are the electronic eigenfunctions and eigenvalues calculated by KS-DFT for the ionic configuration $\{\mathbf{R}_a\}$. The results for $\sigma(\omega)$ (Fig. 7) have estimated relative errors of only 5%–10% (as shown in the figure, both the precision and the accuracy of the calculations are much poorer when only the Γ point is used). The error due to only being able to include a finite number of excited states in Eq. (9) is reflected by the area under the calculated function being 92% of the theoretical value, $\pi e^2 Z\rho_n/2m_e$, where Z is the ionic charge. Figure 7 also shows that the results obtained using four **k** points are fitted very well by a Drude function (the theoretical formula for optical conductivity in nearly free electron metals),

$$\sigma(\omega) = \frac{\sigma}{1+\omega^2\tau^2}, \tag{10}$$

where τ is the relaxation time, and the value of σ so obtained is practically identical to the value obtained by extrapolating the four-**k**-point results to $\omega=0$, $\sigma=0.037\pm0.002$ $(\mu\Omega\ \mathrm{cm})^{-1}$; both agree well with the experimental value,[41] 0.0397 $(\mu\Omega\ \mathrm{cm})^{-1}$.

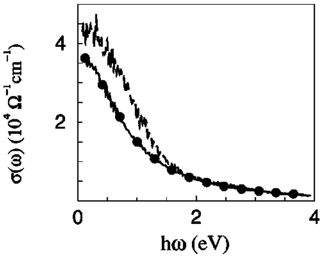

FIG. 7. Optical conductivity of liquid Al at 1000 K, as derived from the Kubo-Greenwood formula: continuous line, results using four special points of the Brillouin zone; dashed line, results using only the Γ point. Solid dots: typical points on the Drude curve fitted to the four-point results.

IV. CONCLUSIONS

In this work we computed static, dynamic and electronic properties of liquid Al near its triple point using a KS-AIMD method. This is the first time that dynamic properties of Al have been obtained other than its self-diffusion coefficient and, via the autocorrelation function of the stress tensor, its shear viscosity coefficient: in this work, as well as the self-diffusion coefficient, we calculated its velocity autocorrelation function, intermediate scattering function, and longitudinal and transverse current correlation functions, which were used to calculate the self-diffusion and shear viscosity coefficients. In particular, the calculated intermediate scattering function gives a dynamic structure factor $S(q,\omega)$ that agrees with experiment better than the results of orbital-free DFT molecular dynamics simulations employing more than twice as many atoms and six times as much simulated time. Thus the use of KS-AIMD to achieve a reliable description of the behavior of liquid metals, including their dynamic properties, is not beyond current computational capacities, at least in the case of simple liquid metals such as Al.

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