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Calculation of the transport properties of liquid aluminum with equilibrium and non-equilibrium molecular dynamics

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Abstract

In this paper, we utilize the techniques of equilibrium and non-equilibrium molecular dynamics to calculate the shear viscosity and the self-diffusion coefficient of liquid aluminum. We use the embedded-atom method potential for these calculations. © 2001 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Computer simulation; Transport properties; Liquid aluminum; Theory and modeling

Introduction

In an effort to minimize research and development time, the casting industry is turning toward a system of computer-aided analysis and prototyping. These advanced casters utilize thermophysical properties such as viscosity and diffusion coefficients to solve numerically the conservation equations for mass, momentum, energy, and solutal concentration of each alloy element. The accuracy and usefulness of these computer models depend critically upon the availability of reliable thermophysical properties of metallic melts. Unfortunately, viscosity data for metals and metallic alloys are sparse. Even the viscosity data for pure liquid metals reported in the literature are quite scattered. Furthermore, the experimental diffusion data are almost non-existent. Therefore the casting engineer relies on either theoretical and correlation models or phenomenological models for their values.

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In the present contribution, we concern ourselves with the application of the method of molecular dynamics (MD) and the embedded atom method (EAM) to calculating the viscosity and diffusion coefficient of a liquid metal, namely Al. For liquid metals, on account of the very large discrepancies in experimental data, it has been recommended that viscosity calculated from theoretical models might be as appropriate as experimental values [1]. To date such theoretical and semiempirical predictions of viscosity have relied on (a) input from experimental pair distribution functions for representing the liquid structure and/or (b) pair potentials for modeling the atomic interactions. The choice of a pair potential cannot be justified for many metallic elements [2]. Apart from first-principle quantum calculations, the EAM many-body interatomic potential represents at this time a realistic way of modeling liquid metals. We show, here, that MD simulations in conjunction with the EAM derived potentials provide a reliable method of predicting transport properties of molten metals.

Model and numerical methods

The many-bodied interatomic potentials based on the EAM methodology of Daw and Baskes [2] have shown great promise for modeling metals. Most of these potentials are parameterized for solid state data. Foiles, however, showed that they are equally valid for the liquid state [3]. There exist a large variety of EAM potentials for pure metals. Here, we use a simple analytical form of an EAM potential for modeling liquid aluminum [4].

We calculate viscosity with two different techniques, namely equilibrium and non-equilibrium molecular dynamics (NEMD). For the equilibrium approach, transport coefficients such as viscosity or diffusivity are calculated by utilizing the linear response theory of Kubo [5]. This theory allows viscosity to be expressed as a time integral of the autocorrelation function for the off-diagonal components of the internal stress tensor. Statistically this approach is sensitive to time origin, thus necessitating very long MD runs for accurate determination of viscosity. To alleviate some of the statistical issues, we employ the method of overlapped data collection for a time-dependent property [6]. The shear stress correlations are overlapped in such a way as to minimize the simulation length and improve the quality of the autocorrelation function. The equilibrium simulations are run under constant energy conditions.

The method of NEMD avoids the large statistical uncertainty inherent to the correlation method. In the NEMD calculation of viscosity, a steady shear-strain rate is applied on the simulation cell. Since periodic boundary conditions are generally used in MD, the boundary conditions in NEMD are modified in order to maintain the spatial integrity of the imposed velocity field. The resulting shear flow gives rise to a shear component of the internal stress tensor, and the coefficient of proportionality between the two is the shear viscosity. At low shear-strain rates (Newtonian regime), NEMD requires very long simulations to alleviate the effect of the noise on the calculation of the stress. Hence, large shear-strain rates are generally used, and the Newtonian shear viscosity is recovered by extrapolating the calculated non-Newtonian viscosity to zero

shear-strain rate. Since the applied shear-strain rate injects energy into the system, thermostats are used to maintain temperature at a constant value. For this, we employ a standard temperature constraint [7]. Details on this thermostat, the NEMD method and algorithm used in the present work can be found in Rappaport [6].

We use an equilibrium approach to obtain the self-diffusion coefficient. For this approach, diffusivity is expressible as the time integral of the autocorrelation function of the velocity [5].

The correlation methods exhibit a strong dependence on the number of particles in the simulation cell with more accurate values obtained with larger systems; in contrast the NEMD displays a weak number dependency, thus significantly smaller systems can be used to obtain accurate results [8]. Hence, on that basis, we report data for a system containing 1372 atoms for equilibrium MD simulations and 256 atoms for NEMD simulations. The simulation cells are cubic with a volume adjusted to correspond to the zero pressure density. The equilibrium MD simulations lasted a minimum of 10^6 to a maximum of 4×10^6 integration time steps with a time step corresponding to 10^{-15} s. For each temperature a series of 20 NEMD simulations, each lasting 32,000 steps with shear-strain rates varying between $1.89 \times 10^{11} \text{ s}^{-1}$ and $1.89 \times 10^{13} \text{ s}^{-1}$, was run.

Since the phenomenon of viscosity in a pure liquid results from the transfer of momentum from an atom to its neighbors, the atomic structure of the computer model should approach as closely as possible the structure of real aluminum. As a test we have verified that the EAM potential we used gives very good agreement between the calculated liquid structure and the experimentally determined pair correlation functions [9].

Results and discussion

Fig. 1 shows the experimental results from a variety of authors [10–14] referenced by Iida and Guthrie [1] along with viscosities calculated with EMD and NEMD. The lower curve at 950 K reports a value of 1.2 mPa s, and the upper curve at the same temperature reports 4.15 mPa s, nearly a 400% variation. The viscosities calculated from the equilibrium and non-equilibrium MD simulations are indicated as filled circles and open squares, respectively. The dashed line is a best fit through the NEMD data. The temperature uncertainty for the equilibrium viscosity is the size of the symbol and arises from the temperature fluctuations in the constant-energy equilibrium simulations. This amounted to ± 10 K. The standard deviation for the calculated equilibrium viscosities was as high as 30%. As a test we increased the number of overlapped correlation functions and found that the average equilibrium viscosities were unchanged and the standard deviation was reduced. On the other hand the NEMD simulations give results with much greater certainty. In that case, the error bars amount to $< 2\%$ and are not shown. The excellent agreement between the equilibrium and non-equilibrium viscosities indicates that the simulation data are representative of the EAM model of aluminum itself and are therefore nearly independent of the method used for their calculation.

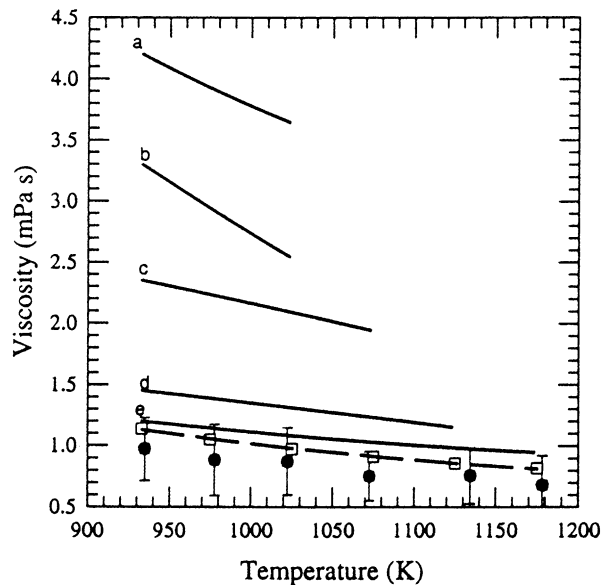


Fig. 1. Viscosity as a function of temperature. The solid lines are experimental data obtained in the 50's and 60's as referenced by Ref. [1] where a, b, c, d, and e correspond with Refs. [10–14], respectively. The open squares are calculated from NEMD. The filled circles are from the equilibrium MD simulations.

In a prior publication, we observed a systematic difference ($\sim 20\%$) for an EAM model of nickel between the viscosity values obtained with non-equilibrium and equilibrium methods [15]. For the lower viscosity aluminum system we observe a similar trend although smaller ($\sim 15\%$). Such a discrepancy has not been observed in the studies of the low viscosity Lennard-Jones liquid [8]. To pinpoint the origin of this discrepancy, we have verified that the time integrator used in the NEMD and EMD does not affect the calculated values of viscosity. Although the NEMD simulations use fewer atoms, we have tested through a series of simulations of liquid aluminum at $T = 1175$ K with 256, 500, and 864 atoms, that the calculated viscosities from NEMD showed no major system size effect which could explain the discrepancy [16]. The NEMD simulations are conducted at constant temperature while EMD simulations are at constant energy. It therefore appears that the only major difference between the results is the fact that in the NEMD the motion of the atoms is constrained by the constant temperature condition. We believe that this may be the reason for the systematic difference with a larger effect for liquids with larger viscosities.

Our data further differs slightly with experiments in its temperature dependence. The temperature dependence of viscosity in liquid metals approximates an Arrhenius relationship of the form: $\eta = A \exp(E/RT)$. From the NEMD viscosity, we estimate the apparent activation energy for viscous flow, E , to ≈ 12.4 kJ mol $^{-1}$, with the prefactor amounting to 0.2293 mPa s. The calculated activation energy is about the same as the activation energy one can determine from most experimental data, with the exception of the higher experimental values that yield activation energies off by up to a factor of 2.

We have also calculated the diffusion coefficients of liquid aluminum. These data are reported in Fig. 2. The temperature variations in the calculated diffusion coefficient amount to the size of the symbol. For these data obtained using the Kubo method, the standard deviations were on the order of 2%. In view of the lack of experimental self-diffusivities, we compare our calculated self-diffusivity data to the diffusivities obtained from Stokes–Einstein, Sutherland–Einstein relations [17], the universal scaling law recently presented by Dzugutov [18], and recent first-principles calculations [19]. The Stokes–Einstein and Sutherland–Einstein relationships relate the diffusivity to the viscosity. We utilized our EMD values for the viscosity to calculate diffusivity from these relations. The universal scaling law for diffusion is obtained as a function of a two-body approximation for the excess entropy, S_2 , where excess entropy is the difference between the entropy of an ideal gas and the entropy of the systems. This two-body approximation is a function of the radial distribution function and thus the diffusion coefficient is dependent only on the structure of the liquid.

The diffusion data we have calculated appear to exhibit Arrhenius behavior. We find the activation energy for the self-diffusivity of liquid aluminum to be -21.33 kJ/mole with the pre-exponential factor being 1.16×10^{-3} cm²/s. The activation energies we obtained compare reasonably well to other theoretical models [20,21].

Comparing the predictions of the Stokes–Einstein and the Sutherland–Einstein models, we notice that the Sutherland–Einstein relationship seems to fit the EMD data

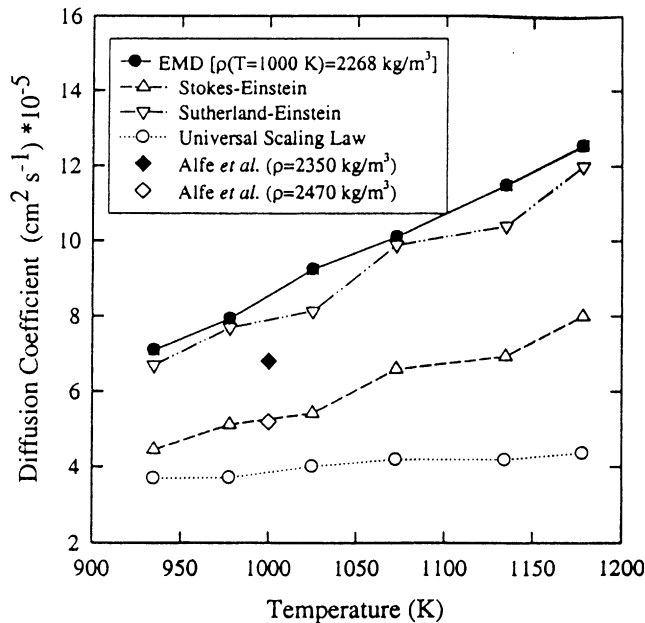


Fig. 2. Diffusivity of liquid aluminum. The filled symbols are calculated with EMD techniques. The diamonds represents the diffusivity calculated by Alfe and Gillan [19] at zero pressure (\diamond) and at experimental (\blacklozenge) densities. The open circles are an application of Dzugutov’s universal scaling law [18]. The open triangles are calculated from hydrodynamic theory utilizing the viscosity data found in Fig. 1 (see text for details).

best. It has been suggested [17] when the radius ratio between the diffusing species and the diffusion medium is approximately equal to one, the Sutherland–Einstein relationship is preferred (i.e. pure substances). The agreement between the Sutherland–Einstein prediction and the EMD results further validates this statement. The Sutherland–Einstein diffusivities are at most about 10% lower than the calculated diffusivities.

The universal scaling law [18] appears to inaccurately describe the temperature dependence of the system with our data. The universal scaling law underestimates the diffusivities over the entire range of temperature. In addition, our system falls into a regime where the universal scaling law may not apply. It appears that the scaling law is valid for values of $-S_2 > 2.0 k_b$. Utilizing the radial distributions obtained with EMD we find that the aluminum system had values for $-S_2$ below $2.0 k_b$ and therefore the universal scaling laws may not be applicable for our system. Furthermore, Yokohama suggests that the three body excess entropy instead of a two-body approximation should be used for liquid metals [22]. Hoyt et al. [23] examined the Dzugutov scaling law using EAM calculations and found that the total excess entropy should be employed and applied for systems described by many-body potentials.

There is a discrepancy in the diffusivity between the first principle simulations and the simulations with Cai and Ye EAM potential. Examining the legend in Fig. 2, we notice that there is a significant difference in the density of our simulations and that of Alfe and Gillan [19]. Our potential predicts a zero pressure density to be about 3.5% below the experimental density while the first principle calculations predict a zero pressure density 5% above experiment. When we sort the densities from low to high it is noticed that the diffusivities are ordered from high to low. The relationship between the density and the diffusivity explains the discrepancy of the data reported in Fig. 2. Thus the zero pressure densities are representative of the potential or model chosen which inadvertently affects the calculated transport properties.

Conclusion

We have computed the viscosity and diffusion coefficients of liquid aluminum by equilibrium and non-equilibrium MD. An EAM potential was used to describe the interactions between the atoms in the liquid metal. The present MD simulations of liquid aluminum illustrate that computations of these transport properties are feasible and reliable. Experimental data for viscosity of aluminum are scattered. Our calculated viscosities were in agreement with the lower limit of the viscosity range. We noted a small effect from the thermostat used in NEMD on the calculated viscosity. This effect appears to be more pronounced for high viscosity fluids. We found that the diffusion data calculated with the EMD method agrees very well with the phenomenological Sutherland–Einstein model. The recently proposed universal scaling law of Dzugutov [18] does not compare favorably with our temperature dependence. At this stage, transport properties calculated with EAM potentials may be as reliable as experimental data and those obtained with first-principle models.

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