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CALCULATION OF VISCOSITY OF LIQUID NICKEL BY MOLECULAR DYNAMICS METHODS

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Introduction

Computer models of casting processes are becoming useful tools in the foundry industry. These models are used to simulate the heat and fluid flows that control the microstructural development of castings. The accuracy and usefulness of these computer models depend critically upon the availability of reliable thermophysical properties of metallic melts. For instance, the simulation of the solidification of metallic alloys includes the numerical solution to the conservation equation for momentum. The viscosity of liquid metals is therefore required in the solution to the momentum equation. Unfortunately, viscosity data for metallic alloys are sparse. Even the viscosity data for pure liquid metals reported in the literature are quite scattered. As an illustrative example, the viscosity of pure Ni, as measured by various investigators may vary by as much as 50% (1). This lack of reliable experimental data and advances over the past decade in assigning credible interatomic potential functions for transition elements are compelling arguments for attempting to predict viscosity liquid transition metals with atomistic computer simulation methods.

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 of a liquid transition metal, namely Ni. For high temperature liquid metals, on account of the very large discrepancies in experimental data, it has been recommended that values of viscosity calculated from theoretical models might be as appropriate as the experimental value (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 transition elements (2). Apart from first-principle quantum calculations, the EAM many-body interatomic potentials represent at this time one of the most realistic ways of modeling liquid transition metals. We show, here, that MD simulations in conjunction with the EAM derived potentials provide a reliable method of predicting viscosity.

Model and Numerical Methods

The EAM of Daw and Baskes (2) leads to a simple accurate many-body representation of the atomic interactions in transition metals. EAM interatomic potentials are essentially parametrized from solid data; however, Foiles showed that they also provide a realistic model of the transition metals in their

liquid state (3). Here, we use a recent analytical form of an EAM potential for modeling liquid nickel (4).

We employ two methods for the calculation of viscosity, namely equilibrium and non-equilibrium molecular dynamics (NEMD). In the equilibrium approach, the calculation of transport coefficients such as viscosity is based on the linear response theory of Kubo (5). In this theory, viscosity is expressible as the time integral of the autocorrelation function of the off-diagonal components of the internal stress tensor. This approach is sensitive to time origin and statistics, thus necessitating very long MD runs for accurate calculation of viscosity. We use the method of overlapped data collection for time-dependent property (6). The samples of shear stress are overlapped to improve the quality of the autocorrelation function without extending the duration of the simulation. 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 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 strain rates (Newtonian regime), the NEMD needs very long simulations to alleviate the effect of the noise on the calculation of the stress. Hence, large strain rates are generally used, and the Newtonian shear viscosity is recovered by extrapolating the calculated non-Newtonian viscosity to zero strain rate. Since the applied shear rate injects energy into the system, thermostats are then used to maintain temperature to a constant value. For this, we employ a standard Nosé thermostat. Details on this thermostat, the NEMD method and algorithm used in the present work can be found in Rapaport (6).

The correlation method exhibits a strong dependence on the number of particles in the simulation cell with more accurate values obtained with large systems; in contrast the NEMD displays a weak number dependency, and significantly smaller systems are needed to obtain good results (7). Hence, on that basis, we have simulated a system containing 1372 atoms for the equilibrium MD simulations and 256 atoms for the NEMD simulations. The simulation cells are cubic with a volume adjusted to correspond to the experimental density (8). The equilibrium molecular dynamics simulations lasted a minimum of 10^6 to a maximum of 4×10^6 integration time steps with a time step corresponding to 10^{-16} s. For each temperature a series of 10 NEMD simulations each lasting 32,000 steps with strain rates varying between 1.28×10^{13} and 8.2×10^{12} 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 nickel. 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

In Figure 1, we report our results as well as the experimental viscosity of liquid Ni as determined by various investigators. The unlabelled solid curves are reported in Iida and Guthrie (1) from original sources of the early 1960s. The solid lines labeled "a" and "p" are from references 10 and 11. The viscosity calculated from the equilibrium and nonequilibrium 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 associated with the equilibrium viscosity arises from the temperature fluctuations in the constant-energy equilibrium simulations. The standard deviation of the equilibrium
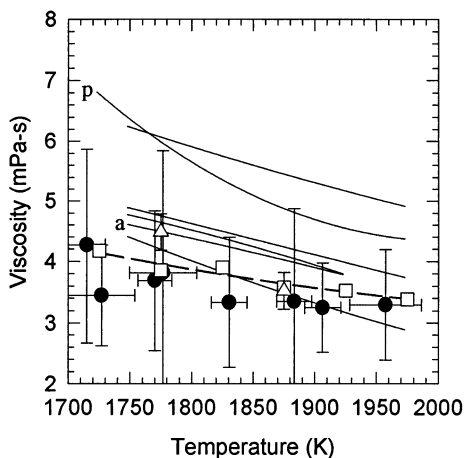
Figure 1. Viscosity as a function of temperature. The solid lines are experimental data (see text for details). The open squares are calculated from NEMD. The filled circles are from the equilibrium MD simulations. The open triangles are the MD results of reference 12.

viscosity is as much as 50%. We note large variations in this standard deviation, which is attributed to simulations of variable time lengths and therefore variable number of stress auto-correlation functions used in the calculation of the equilibrium viscosity.

On the other hand the NEMD simulations give results with much greater certainty. In that case, the error bars amount to less than 2% and are not shown. Although the equilibrium MD data appears to be systematically lower than the NEMD viscosities, we do not believe in view of the large error bars in the former that this observation is significant. Therefore, the good agreement between the equilibrium and non-equilibrium viscosity indicates that the simulation data are representative of the EAM model itself and are therefore independent of the method used for their calculation. However, the small difference between the two sets of data warrants further investigation in the systematic error that may be introduced by the extrapolation of the NEMD to low strain rates.

A comparison between the calculated and measured viscosity is made difficult by the large discrepancies in the experimental data. The viscosity of high temperature liquid metals is a thermo-physical property difficult to measure experimentally. Only a few experimental methods exist for measuring the viscosity of liquid metals (1). The oscillating-vessel method is most frequently used in measuring viscosity at elevated temperatures. The determination of viscosity from the damping of the vessel oscillations necessitates a back calculation and therefore the use of an analytical mathematical model of the oscillating system. Many secondary effects such as surface tension, slippage at the liquid/vessel interface, convection, etc. . . need to be accounted for in this model. However, due to the difficulty in solving analytically for the damped oscillations, approximate formulae are often used resulting in discrepancies, between the experimental results of different workers, as large as 50%. Although the present calculated viscosity differs from most of the experimental data, it is gratifying to note that it agrees with some as seen in Figure 1.

Our data further differs 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 viscous flow, E, to approximately 1.30 kJmol^{-1}. The prefactor amounts to 0.8435 mPa.s. The calculated activation energy is lower than the activation energy one can determine from most experimental data by nearly a factor 1.5. The best agreement with experimental data is obtained with the measurements of reference 11.

Finally, a recent publication (12) reported MD calculations of the viscosity of liquid Ni using a Voter-Chen EAM potential (13). We present in Figure 1 the Green-Kubo equilibrium MD viscosities of their study. These two viscosities compare reasonably well with our data. Unfortunately the simulations reported in that paper differ with ours not only in the EAM potential used but also in the density. It is therefore impossible to separate these effects.

Conclusion

We have calculated theoretically the viscosity of liquid nickel by equilibrium and non-equilibrium MD. The interactions between atoms in the liquid transition metal are modeled via many-body potentials derived with the embedded atom method. The present molecular dynamics simulations of liquid nickel demonstrate that viscosity of high temperature liquid metals can be calculated reliably. The calculated viscosity is shown to be independent of the numerical method used (i.e. equilibrium MD versus NEMD) and characteristic of the EAM model itself. In contrast to the equilibrium MD, the NEMD presents the advantage of computational efficiency and accuracy. The calculated viscosity and the activation energy are comparable to some of the existing experimentally determined data. However, the large discrepancies in the measured viscosity render the comparison between experimental and our numerical data difficult. In view of the large discrepancies in measured and calculated viscosity of Ni and the fact that most of the experimental viscosity data date back to the 1960s and early 1970s, an experimental re-examination of the viscosity of liquid nickel would certainly be in order.

Acknowledgments

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