Improvement of computer simulation models for metallic melts via quasielastic neutron scattering: A case study of liquid titanium

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A combination of quasielastic neutron scattering (QNS) and molecular-dynamics (MD) simulation is used to modify an embedded atom method (EAM) potential for Ti with respect to the description of melt properties and crystallization from the melt. In the MD simulation, the EAM model is optimized such that agreement with accurate data of self-diffusion coefficients from QNS is achieved. As a result the density and the melting temperature are in good agreement with experiment.

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I. INTRODUCTION

The investigation of metallic liquids and their crystallization from the melt provides a great challenge to experiment and modeling.[1,2] Metallic systems typically solidify in a temperature range between 1000 and 2000 K where it is elaborate to carry out experiments on the structure and dynamics of the melt as well as the crystallization process.

The modeling of metallic melts via particle-based simulation techniques such as molecular dynamics (MD) suffers from the small experimental database. For this reason, most of the model potentials, that have been developed to describe the effective interactions between the atoms in a metal, have been parameterized with respect to properties of crystalline phases. These potentials often reproduce reliably on a qualitative level various melt properties, such as, e.g., different aspects of transport and structural relaxation.[3–6] However, they show systematic quantitative deviations with respect to the temperature dependence of density, structural quantities, mass transport coefficients, and the value of the melting temperature.[7–12]

In this Brief Report, we show for the example of liquid Ti how an existing potential can be improved using quasielastic neutron-scattering (QNS) data as a reference. The potential, considered here, has been proposed by Zope and Mishin[13] (in the following referred to as ZoM model). This potential has been fitted to various zero-temperature properties of α-Ti (hcp phase) that were obtained from *ab initio* calculations. Zope and Mishin have shown that it leads to a good agreement with experiment with respect to the high-temperature bcc phase of Ti (β-Ti).[13] Below we present a simple strategy how one can modify the ZoM model (and possibly similar model potentials for metals) to describe various properties of the melt more accurately, including the location of the melting transition. The basis are accurate measurements of the temperature dependence of the self-diffusion coefficient of the melt.

The present work combines state-of-the-art QNS experiments with MD simulation. We demonstrate that the temperature dependence of the self-diffusion coefficient, D_{Ti}, is an appropriate feature to adjust an effective potential to experimental data. As a basis for that, a model potential is required that already describes correctly certain trends of the materials properties. Then, the QNS data can be used to calibrate the temperature scale of the potential (see below). Realistic potentials for MD simulations are an important requirement for the study of solidification processes in metallic melts. In particular, interfacial properties such as interfacial free energies are in general not accessible from experiments nor from *ab initio* simulations (due to the limitation of system size and time scale). In MD simulations with effective potentials, such properties can be calculated[1,12] and thus, they are a very valuable tool toward a microscopic understanding of crystal growth and nucleation in metallic melts.

II. MODIFICATION OF THE POTENTIAL

The aforementioned ZoM potential has been derived in the framework of the embedded atom method (EAM).[14] In this framework, one introduces an embedding function $F_i(\rho_{\mathrm{h},i})$ that depends on the host electron density $\rho_{\mathrm{h},i}$ at atom i. The function F_i describes the energy to embed an atom i into the local electron gas due to the other atoms in the system. It is assumed that the host electron density $\rho_{\mathrm{h},i}$ at atom i can be approximated by a linear superposition of pairwise contributions that depend on the distance $r_{ij}=|\vec{r}_i-\vec{r}_j|$ between atoms i and j at positions $\vec{r}_i$ and $\vec{r}_j$, respectively. The total EAM energy of the system, V, is given by the contributions $F(\rho_{\mathrm{h},i})$ and additional pair interaction terms $u(r_{ij})$ that describe the short-ranged hard-core repulsion between the atoms, $V=\Sigma_{i=1}^{N}F(\rho_{\mathrm{h},i})+\frac{1}{2}\Sigma_{i=1}^{N}\Sigma_{j\neq i}^{N}u(r_{ij})$ (with N the total number of atoms in the system). The details of the ZoM potential for Ti can be found in the original publication.[13]

In order to improve the ZoM potential, we multiply the whole EAM potential by a constant α such that the new EAM energy V' is related to the old one by $V'=\alpha V$. As an optimal value for α, we found $\alpha=1.245$ (in the following we refer to the corresponding modified potential as the Mod-ZoM potential). This value was determined by performing MD simulations with different values of α and choosing the value that leads to the best agreement with the self-diffusion data, as obtained by QNS. As we shall see below, the introduction of the parameter α yields essentially an adjustment of the temperature scale, keeping, e.g., properties unchanged that are defined relative to the melting temperature such as crystal-growth coefficients.

III. EXPERIMENTAL TECHNIQUES

QNS in combination with electromagnetic levitation has been recently established for the investigation of the dynamics of metallic melts.[15] Using these techniques, self-diffusion coefficients can be determined with high accuracy, provided that at low wave numbers q the total scattering signal is dominated by incoherent-scattering contributions. The latter requirement is fulfilled in metallic melts containing, e.g., Ni, Co, or Ti. So far, QNS on levitated samples has been, in particular, used to measure the self-diffusion coefficients of Ni in pure Ni,[15] Zr-Ni,[16,17] and silicon-rich Si-Ni.[18]

The QNS measurement of the self-diffusion constant of Ti, D_{Ti}, was performed at the neutron time-of-flight spectrometer TOFTOF (Ref. 19) of the FRM II. An electromagnetic levitation device, especially designed for neutron spectroscopy,[15] was applied. The roughly spherical, electrically conductive Ti sample, 10 mm in diameter with a mass of 1.7 g, was levitated by an inhomogeneous electromagnetic radio frequency field in a purified 650 mbar Ar/He atmosphere. The temperature was measured contact free with a two-color pyrometer with a precision on the order of ± 5 K. The data-acquisition time was 100 min for each considered temperature in the range $2110 \geq T \geq 1953$ K.

A wavelength of the incident neutron of 5.4 Å gives access to a wave number q ranging from 0.3 to 2.2 Å^{-1} at zero energy transfer. The instrumental energy resolution function was measured at 300 K using a vanadium standard of similar size. It was well fitted by a Gaussian function with a full width at half maximum of ≈ 80 μeV. After the correction for the empty sample environment, the self-absorption, and the detector background, the double-differential cross section was obtained, $\frac{\partial^2\sigma}{\partial\Omega\partial\hbar\omega}=\frac{1}{4\pi}\frac{k_{\mathrm{f}}}{k_i}[\sigma_{\mathrm{inc}}S_{\mathrm{s}}^*(q,\omega)+\sigma_{\mathrm{coh}}S_{\mathrm{coh}}^*(q,\omega)]$, with Ω the solid angle, $\hbar\omega$ the energy transfer, k_i the wave number of the incident neutrons, k_{f} that of the scattered neutrons, and q the momentum transfer. σ_{inc} is the incoherent-scattering cross section and σ_{coh} is the coherent-scattering cross section. The functions $S_{\mathrm{s}}^*(q,\omega)$ and $S_{\mathrm{coh}}^*(q,\omega)$ denote, respectively, the incoherent and coherent parts of the dynamic structure factor that result from the measurement.

In the case of Ti, the scattering cross sections are given by $\sigma_{\mathrm{inc}}=2.87$ b and $\sigma_{\mathrm{coh}}=4.35$ b.[20] Well below the location of the first peak in the static structure factor at $q \approx 2.65$ Å^{-1},[21,22] the signal is dominated by the incoherent contributions and thus information about the self-motion can be extracted in this q range. Therefore, Fourier deconvolution of $S^*(q,\omega)$ yields the time-dependent incoherent intermediate scattering function $S_{\mathrm{s}}(q,t)$. In the hydrodynamic limit, $S_{\mathrm{s}}(q,t)$ follows an exponential decay of the form[23]

$$f(q,t) = a_q \exp(-t/\tau_q) \tag{1}$$

with a_q an amplitude and τ_q a relaxation time, both depending on wave number q. In the hydrodynamic regime, D_{Ti} is related to the relaxation time by $1/\tau_q = D_{\mathrm{Ti}}q^2$. We have employed this formula to extract D_{Ti} from the QNS data, as shown below.

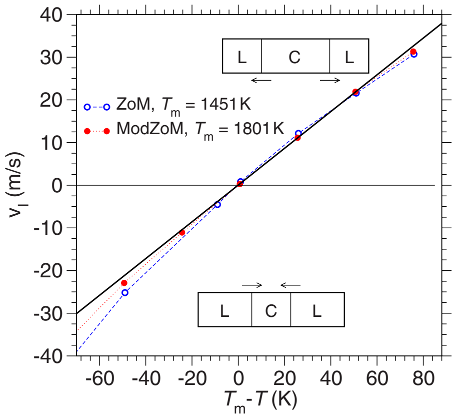

FIG. 1. (Color online) Interface velocity, v_{I}, as a function of undercooling, $T_{\mathrm{m}}-T$, for the two simulation models. The indicated values for T_{m} are estimated from the condition $v_{\mathrm{I}}(T_{\mathrm{m}})=0$. The two sketches illustrate the direction of the crystal("C")-liquid("L") interface motion at negative and positive interface velocity, respectively.

IV. MELTING TEMPERATURE AND CRYSTAL-GROWTH COEFFICIENT

To estimate the melting temperature of the ZoM and the ModZoM models, MD simulations of an inhomogeneous solid-liquid system were performed. For the integration of the equations of motion, a velocity Verlet algorithm[24] was employed using a time step of about 1 fs. Systems of $N=33\,750$ particles in a simulation box of nominal size $L \times L \times 5L$ with periodic boundary conditions in all directions were considered where with respect to the z-direction crystalline β-Ti in the middle of the simulation box is surrounded by the liquid and separated from it by two solid-liquid interfaces (considering in this work only the 100 orientation of the crystal). The simulations were done at zero pressure, $p=0$, both in the NpT and the Np_zT ensemble, with p_z the pressure in z direction. At each temperature, eight independent samples were simulated. More details about the preparation of the inhomogeneous solid-liquid system, the length of the simulation runs, etc., can be found in Ref. 12 where we have done a similar analysis for a model of Ni.

The melting temperature is obtained by determining the velocity v_{I} with which the interfaces move at different temperatures. The interface velocity v_{I} measures the speed with which the crystal grows. For $T>T_{\mathrm{m}}$, the crystal melts and so $v_{\mathrm{I}}<0$ whereas below T_{m} the crystal grows with $v_{\mathrm{I}}>0$ (see the sketches in Fig. 1). Thus, the melting temperature T_{m} is found by the extrapolation $v_{\mathrm{I}} \to 0$. In the vicinity of T_{m}, one expects a linear relation of v_{I} as a function of undercooling, $v_{\mathrm{I}}=k_{100}(T_{\mathrm{m}}-T)$ with k_{100} the kinetic growth coefficient for the crystal's 100 orientation, considered here.

Figure 1 displays v_{I} as a function of undercooling, $T_{\mathrm{m}}-T$. As we see, the slope of v_{I} is similar for the ZoM and the ModZoM models. A linear fit to the data for v_{I} (solid line) yields $k_{100}=0.42$ m/s/K for the kinetic coefficient. This shows that relative to T_{m} the growth kinetics is not changed using the modified model. However, the melting temperatures are very different for the two models, giving T_{m}

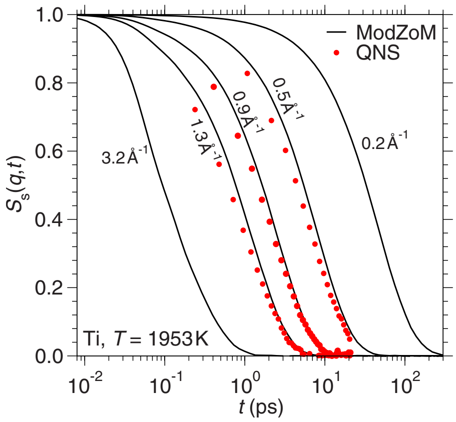

FIG. 2. (Color online) Incoherent intermediate scattering functions $S_{\rm s}(q,t)$ for different values of q, as indicated. Shown are MD results using the ModZoM model (solid lines) and results from QNS experiments (circles).

$=1451$ K for the ZoM model and $T_{\rm m}=1801$ K for the ModZoM model. Thus, the ModZoM model yields a much better agreement with the experimental value, $T_{\rm m}=1941$ K,[25] than the original ZoM model. This is very remarkable since we have not modified the ZoM model with respect to $T_{\rm m}$ but with respect to the self-diffusion constants from the QNS measurements.

V. SELF-DIFFUSION COEFFICIENT

Additional MD simulations in the temperature range $2170 \geq T \geq 1400$ K were done for the calculation of dynamic properties. Systems of $N=1500$ particles in a cubic simulation box were considered. At each temperature, they were equilibrated for 2×10^5 MD steps in the NpT ensemble (with a time step of 1.5 fs), before production runs over 5 million MD steps in the microcanonical ensemble commenced.

The incoherent intermediate scattering function $S_{\rm s}(q,t)$ was calculated from the MD trajectories via $S_{\rm s}(q,t) =N^{-1}\langle\sum_{k=1}^{N}\exp\{i\vec{q}\cdot[\vec{r}_k(t)-\vec{r}_k(0)]\}\rangle$ [with $\vec{r}_k(t)$ the position of particle k at time t].[23] Figure 2 shows this correlation function for several values of q at $T=1953$ K. The results for the ModZoM potential are in very good agreement with the QNS measurements.

The long-time decay of $S_{\rm s}(q,t)$ can be well fitted by an exponential function, as given by Eq. (1), from which the relaxation time τ_q can be extracted. In Fig. 3, $1/\tau_q$ is plotted as a function of q^2 at $T=1953$ K. Up to about $q=1.2$ Å^{-1} both QNS data and simulation (with the ModZoM) model agree very well and follow nicely a q^2 behavior, as expected in the hydrodynamic limit. That the data are indeed in agreement with the hydrodynamic prediction is indicated by the solid line which shows $D_{\rm Ti}q^2$, where $D_{\rm Ti}$ is the estimate from the MD simulation at $T=1953$ K, as calculated independently from the mean-squared displacement via the Einstein relation.[23]

An Arrhenius plot of the self-diffusion constant is shown in Fig. 4. Also included in this plot are the data for $D_{\rm Ti}$, as obtained from MD simulation with the ZoM model. Whereas the ZoM model overestimates the QNS data[26] by about 50%, the ModZoM model yields almost quantitative agreement with the experiment.

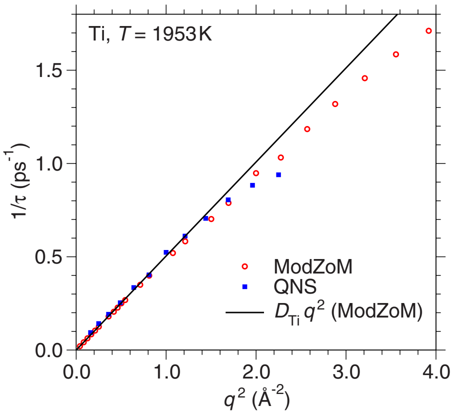

FIG. 3. (Color online) Inverse relaxation time, $1/\tau$, at the temperature $T=1953$ K as a function of q^2 for the MD with the ModZoM model (open circles) in comparison to the QNS data (filled squares). The dashed line shows the function $f(q)=D_{\rm Ti}q^2$, using the value $D_{\rm Ti}=5.04\times10^{-9}$ m^2/s, as obtained from the MD with the ModZoM model.

In the inset of Fig. 4, the temperature dependence of the total mass densities, $\rho(T)$ as obtained from the NpT simulations for the ZoM and ModZoM models, are shown in comparison to experimental data by Iida and Guthrie ("E1") (Ref. 27) and by Watanabe *et al.* ("E2").[28] Although the shape of the potential is not modified by the factor α, the density of the ModZoM model is different from that of the ZoM model because the simulations are performed at constant pressure ($p=0$). As can be inferred from the figure, the simulation with the modified potential yields a very good agreement with experiment whereas the mass density from the original ZoM model underestimates the experiment by about 2–3 %. Also here we emphasize that we have not modified the ZoM model with respect to the density but with respect to the self-diffusion constants.

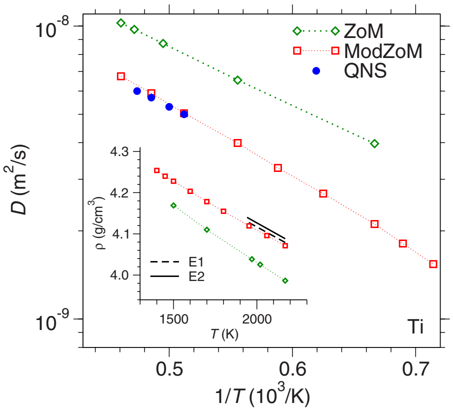

FIG. 4. (Color online) Arrhenius plot of the self-diffusion constant, as obtained from the MD simulations with the ZoM and the ModZoM models, in comparison to QNS. In the inset, the temperature dependence of the density from the simulation is compared to experimental data by Iida and Guthrie (E1) (Ref. 27) and by Watanabe *et al.* (E2) (Ref. 28).

VI. CONCLUSIONS

QNS in combination with electromagnetic levitation allows to study the dynamics of refractory metallic melts at high temperatures. Here, we have demonstrated how this technique can be used to modify interaction potentials (e.g., of the EAM type) such that a realistic modeling of various melt properties is achieved, including the location of the melting transition. To this end, self-diffusion coefficients at different temperatures, as measured by QNS, provide an appropriate database. If already good potentials are available (as in our case the ZoM potential[13] for Ti), then the multiplication of the potential function by a constant factor can already lead to a very good agreement with experiment.

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