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Accurate melting temperatures for Ne nanoclusters and bulk from an effective two-body potential via molecular dynamics simulations

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ABSTRACT

We have calculated the melting temperatures for Ne nanoclusters and bulk solid using two-body Hartree–Fock dispersion (HFD)-like potential by molecular dynamics simulations. To take quantum and many-body forces into account, a new simple and accurate empirical expression is used with the HFD-like potential without requiring expensive calculations. The results indicate that our effective HFD-like potential improves the prediction of the classical two-body results to get better agreement with experiment than an ab initio model.

1. Introduction

Melting is a phenomenon that is still under intensive investigation. Although the thermodynamic basis of phase equilibrium is well understood, the accurate prediction of melting points provides a severe test for statistical mechanical theories and our knowledge of intermolecular potentials [1,2]. Predicting melting points is also a nontrivial task. The standard computational method relies on analyzing the different properties of the solid phase (such as energy, volume, heat capacity, and radial distribution function) during melting obtained from molecular dynamics (MD) or Monte Carlo (MC) simulations. An alternative idea is to obtain information about the melting transition by studying finite clusters and extrapolating the results to infinitely large systems [3]. We have been considered the both approaches in this work.

Neon is a noble gas, has closed electron shells, and it crystallizes only in a face-centered cubic structure. Because of its simplicity, neon seems to be an ideal test system for the theoretical methods (such as MD simulation) [4].

Holt et al. [5] considered the quantum mechanics computations in MC simulation for solid neon and found that quantum corrections are large (6–25%) for solid properties even at the triple point. Also, Solca et al. [6] determined the melting curve of neon in good agreement with experimental data using ab initio pair potentials and the inclusion of quantum effects. Based on these prior studies, it is clear that quantum effects cannot be ignored for solid neon and that the neglect of these effects will lead to discrepancies when experimental data and classical results are compared.

It is also well known that three-body interactions can make a small but significant contribution to properties of solids [7]. To obtain a quantitative agreement with experiment, pair potentials must be used in conjunction with three-body interactions [8–11]. There are many contributions to three-body interactions, but evidences [7] indicate that the triple-dipole term of Axilrod and Teller (AT) [12] is a fairly good approximation. Nonetheless, the need for three-body calculations, in addition to pair calculations, represents a considerable computational impediment. Solca et al. [6] determined melting curve of neon from nonequilibrium MD simulations using ab initio pair-potentials and inclusion of three-body effects at constant pressure. Pahl et al. [10] also calculated accurate melting temperatures for neon and argon using ab initio potentials and inclusion of AT three-body expression by studying finite clusters and extrapolating the results to infinitely large systems. Schwerdtfeger and Hermann [11] performed quantum ab initio calculations for neon triplet and subsequently adjusted the resulted data to an extended triple-dipole AT potential. They concluded that the more complete treatment of three-body force and the four-body force should be considered.

The role of the many-body forces has not been completely understood in the solid properties such as the melting point [9]. Therefore, we have calculated the melting temperatures of nanoclusters and bulk solid neon using a two-body Hartree–Fock

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Table 1
The HFD-like parameters of neon used in this work.

Parameter	Value
ε/k (K)	42.25
σ (Å)	2.759
A^*	2.0342 × 104
a^*	10.3929
$C_6{}^*$	1.2839
$C_8{}^*$	7.8407
$C_{10}{}^*$	−8.2396
b_0	0.1277
b_1	−0.0181
b_2	0.0008
b_3	-1.3415×10^{-5}

dispersion (HFD)-like potential by MD simulation. To take quantum and many-body forces into account, a new simple and accurate empirical expression is used with the HFD-like potential without requiring an expensive three-body calculation.

2. Intermolecular potentials

Systems of spherical molecules, such as the rare gases, have been intensively and successfully studied over a broad range of temperatures and densities using pair interactions of HFD-like model [13–16]. Therefore, the reduced HFD-like potential has been used as a classical two-body potential for neon which has been obtained via the inversion of reduced viscosity collision integrals at zero pressure [15]:

$$U_{2B}^* = A^* \exp(-a^* x) - \left(\frac{C_6^*}{x^6} + \frac{C_8^*}{x^8} + \frac{C_{10}^*}{x^{10}}\right) \quad (1)$$

where $x = r/\sigma$ and $U_{2B}{}^* = U_{2B}/\varepsilon$. The values of the parameters of the HFD-like potential for neon have been given in Table 1.

Hauschild and Prausnitz [17] proposed a many-body correction term in conjunction with the two-body Kihara potential which was a field term proportional to the 9/10 power of the overall density ($\rho^{0.9}$) as well as to the attractive-energy contribution from the two-body potential ($U_{2B\text{-}Att}$):

$$U_{HP}^* = \alpha \left(\frac{\rho}{\rho_C}\right)^{0.9} U_{2B\text{-}Att}^* \quad (2)$$

where α is an adjustable parameter and ρ_c is the density at the vapor–liquid critical point.

Abbaspour et al. [18–20] have proposed the modified Hauschild and Prausnitz three-body potential in which temperature and density dependence of the coefficient α determined for different pure and mixture fluid systems. This three-body potential was proportional to the attractive-energy contribution from the two-body potential, but it has been demonstrated that the accurate properties of the solids may be well described using the effective two-body potential (with a specially adjusted short-range correcting term) instead of the only three-body exchange interaction. Therefore, we have introduced the following correction term, in conjunction with the classical two-body HFD-like potential, which is a field term proportional to the both repulsive and attractive energy contribution from the two-body potential:

$$U_{MB}^* = \beta U_{2B}^* \quad (3)$$

where β is an adjustable parameter which is dependent to the temperature at constant pressure (according to the work of Hauschild and Prausnitz [17]).

We have determined the adjustable parameter β by comparison between prediction of internal energy of perfect solid neon ($T \leq 24$ K) at different temperatures (at constant pressure) and experimental data [21] and fitted to the following equation and presented in Fig. 1:

$$\beta = \sum_{i=0}^{3} b_i T(K)^i \quad (4)$$

The values of the parameters of Eq. (4) have been also given in Table 1. The β value for the temperatures above the melting

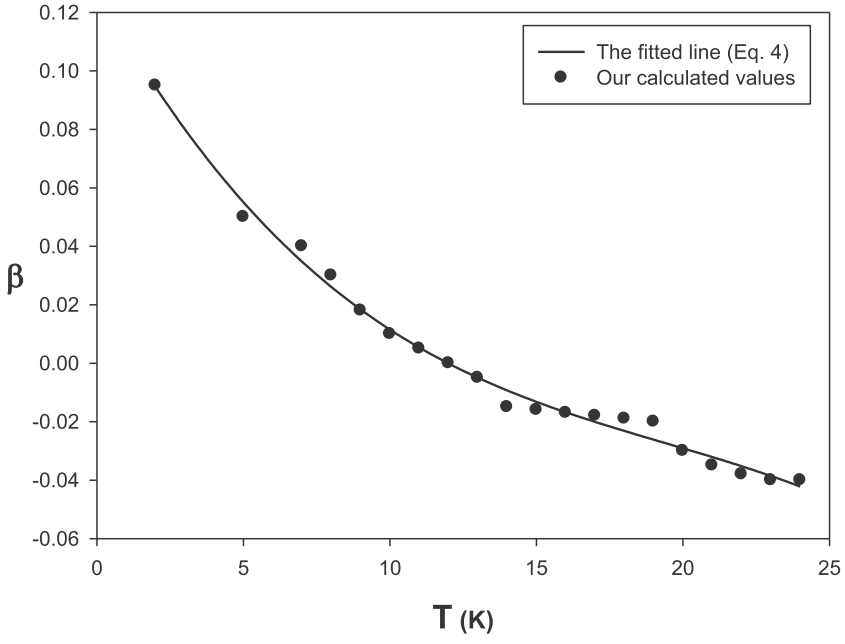

Fig. 1. Our calculated β values at different temperatures and the fitted line for solid neon.