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Numerical simulations of the melting behavior of bulk and nanometer-sized Cu systems

G. Manai[a], F. Delogu[b],*

[a]*Department of Physics, Trinity College, Dublin 2, Ireland*
[b]*Dipartimento di Ingegneria Chimica e Materiali, Università degli Studi di Cagliari, piazza d'Armi, 09123 Cagliari, Italy*

Abstract

Molecular dynamics simulations have been employed to investigate the melting mechanisms of four different Cu systems consisting of a surface-free crystalline bulk, a semi-crystal terminating with a free surface and two unsupported particles with a radius of about 4 and 8 nm, respectively. Starting from a relaxed configuration at 300 K, the systems were gradually heated up to the characteristic melting points. The surface-free bulk system underwent homogeneous melting at the limit of superheating, whereas the melting of the semi-crystal and of the nanometer-sized particles occurred with heterogeneous features. In these latter cases, the structural and energetic properties revealed a two-state character with a definite difference between disordered surface layers and bulk-like interiors. In addition, the melting point and the latent heat of fusion of the nanometer-sized particles were significantly depressed with respect to the ones of the semi-crystal, approximately corresponding to the equilibrium values. Pre-melting phenomena took place at the free surfaces at temperatures significantly below the melting point, determining the formation of a solid–liquid interface. Numerical findings indicate that in all the cases the onset of melting is connected with the proliferation and migration of lattice defects and that an intimate relationship exists between homogeneous and heterogeneous melting mechanisms.

1. Introduction

The study of systems with characteristic size on the nanometer scale represents today an exciting area of fundamental research with remarkable technological relevance due to the novel physical and chemical behavior appearing at such level [1,2]. For example, in the mesoscale regime between small atomic clusters and infinite bulk systems the physical and chemical properties undergo a smooth regular variation generally described by a power-law scaling with the system size [1–4], which replaces the irregular behavior underlying the so-called "magic numbers" [5]. A typical consequence of smooth size effects is represented by the depression of the melting point of small particles, theoretically predicted in 1909 [6] and experimentally observed decades later [7–10]. Although the decrease in the melting point with decrease in the particle size can be satisfactorily explained on a phenomenological basis by the size dependence of the chemical potential of atoms and molecules in finite systems [6,11–16], the insight into the atomic-scale processes underlying such behavior is still limited. The evidence that not only the melting point but also the latent heat of fusion is depressed [17–20] is a further demonstration that the whole thermodynamic behavior is affected.

The dependence of thermodynamic properties on the system size can be in principle exploited to throw light on the atomic-scale mechanisms governing the occurrence of melting, not yet understood [21]. The comparison of the transition behavior of bulk systems and particles could

*Corresponding author. Tel.: +39 070 675 50 73;
fax: +39 070 675 50 67.

E-mail address: delogu@dicm.unica.it (F. Delogu).

indeed point out unexpected connections between the apparently uncorrelated melting processes undergone at different temperatures. Experimental, numerical and theoretical evidences indicate that the solid–liquid transition can occur with either homogeneous or heterogeneous mechanisms depending on the suppression of surface effects [22–27]. Despite various criteria have been proposed starting from the beginning of the XX century [21,23,28–30], a comprehensive theoretical approach able to rationalize the different features of melting processes is still lacking. The successful connection between melting and topological defects established for two-dimensional systems by the so-called KTHNY theory [31–33] suggests, however, that a similar mechanistic scenario could also apply to the case of three-dimensional systems [21,23], for which a dislocation-mediated melting mechanism is invoked [21,23,34–36].

Along this line of inquiry, the present work attempts to investigate by molecular dynamics (MD) the melting mechanism of bulk systems with and without a free surface as well as of particles in the mesoscale regime. Attention is focused on the identification and characterization of lattice irregularities and defects, the amount of which is used to compare the homogeneous and heterogeneous melting processes occurring, respectively, in surface-free bulk systems and in semi-crystals and particles. The details of calculations, which take advantage of previous studies [21,23,27,35–45], are described in the following.

2. Computational methods

Numerical simulations were carried out on Cu systems. Interatomic forces were described by a semi-empirical tight-binding (TB) potential based on the second-moment approximation to the electronic density of states [46–48]. The values of the potential parameters were taken from the literature [48]. Interactions were computed within a cutoff radius approximately corresponding to the seventh shell of neighbors. Although a cutoff distance including the fifth neighbors is sufficient to satisfactorily reproduce the thermodynamic properties [48], its extension to the seventh shell permits to improve the simulation of the elastic behavior with an acceptable increase in computational time.

The semi-empirical TB potential, while describing remarkably well the atomic interactions in the bulk [46–48], is not particularly suited for simulating surface properties. In this regard, the Finnis–Sinclair potential [49] and the so-called embedded-atom-method [50] are more versatile. In spite of this, the TB force scheme permits accurate simulations of both face-centered-cubic (FCC) and hexagonal-close-packed (HCP) metallic structures [46–48]. The TB potential represents then a natural choice for studying FCC metals despite the possible drawbacks in the evaluation of surface properties. Furthermore, the present study is not aimed to quantitatively predict the physical and chemical behavior of Cu systems, but rather to investigate the melting mechanism on a qualitative basis. Under such circumstances, the accurate reproduction of

surface properties can be regarded as a secondary objective.

Simulations were carried out within the so-called Nosè–Andersen (*NPT*) ensemble with the number of atoms *N*, the temperature *T* and the pressure *P* constant [51,52]. The so-called Parrinello–Rahman scheme, allowing for the correct simulation of changes in the crystallographic cell shape, was also implemented [53]. The equations of motion were solved by applying a fifth-order predictor–corrector algorithm [54] with a time step δt equal to 2.0 fs.

The long-range structural order within the different bulk systems was investigated by means of the conventional two- and three-dimensional static order parameters $S_p(\mathbf{k})$ and $S(\mathbf{k})$ [27,40,41,54]. The pair correlation function (PCF) was also employed [54]. The well-known relationship between potential energy *U* and structural order was exploited to follow the gradual thermal disordering and the final collapse of the crystalline structures [37,40,41,44,45].

The local crystalline order was characterized by means of the so-called Honeycutt–Andersen (HA) parameters [39], which also permit the identification of stacking faults. Local lattice distortions were further characterized by identifying the atoms with defective coordination, i.e. with a number of nearest neighbors different from 12. This latter quantity was evaluated for each atom by applying a distance criterion. Two atoms were accordingly regarded as nearest neighbors when located at distances shorter than the one, r_{min}, corresponding to the first minimum of the PCF [35,36]. Information on point and linear lattice defects such as vacancies, interstitials and dislocations was obtained by studying the spatial correlation between the atoms with defective coordination. The connected structures they formed were identified on the basis of the same distance criterion used to evaluate the coordination number [35,36]. Two atoms with defective coordination were thus regarded as belonging to the same cluster when their distance was shorter than r_{min}. This permitted to estimate the number N_{cl} of clusters and their size *n*.

Lattice defects were identified by means of the direct visualization technique based on the coordination number generally employed in numerical simulations [55].

3. Homogeneous melting of a surface-free bulk system

The stability of a superheated crystalline phase is limited by a hierarchy of internal energy- [56], entropy-, enthalpy- and volume-driven instabilities [24]. The homogeneous nucleation of the molten phase in the crystalline bulk represents the crucial process establishing the maximum limit of superheating T_m^K [25]. Such limit can be easily attained in numerical studies by simulating the behavior of a defect- and surface-free crystalline bulk, obtained by applying periodic boundary conditions (PBCs) along the three Cartesian directions [54].

Calculations were performed on a system of 6912 atoms arranged in the FCC cF4 lattice. The system was initially relaxed at a temperature $T = 300$ K and an external