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Statistical distribution of thermal vacancies close to the melting point

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ABSTRACT

A detailed description of the statistical distribution of thermal vacancies in an homogeneous crystal near its melting point is presented, using the embedded atom model for copper as an example. As the temperature increase, the average number of thermal vacancies generated by atoms migrating to neighboring sites increases according to Arrhenius' law. We present for the first time a model for the statistical distribution of thermal vacancies, which according to our atomistic computer simulations follow a Gamma distribution. All the simulations are carried out by classical molecular dynamics and the recognition of vacancies is achieved via a recently developed algorithm. Our results could be useful in the further development of a theory explaining the mechanism of homogeneous melting, which seems to be mediated by the accumulation of thermal vacancies near the melting point.

1. Introduction

Understanding the production of thermal vacancies due to atomic migration near the melting temperature T_m is a key element for a theory of homogeneous melting (i.e. without taking into account the effect of surfaces). Recently it has been shown [1] that, at high enough temperatures, even the formation of small aggregates of thermal vacancies and interstitials can trigger melting in an homogeneous crystal. Moreover, recent studies involving computer simulation of simple crystals with periodic boundary conditions [2–6] have connected the catastrophic collapse of the crystal in homogeneous melting to a collective (*ring*-like) movement of atoms due to thermally produced vacancies. In order to construct a quantitative model, however, there is a key piece missing: the statistical distribution of thermal vacancies at a given temperature T.

For temperatures close to T_m, the expected concentration of vacancies $\langle f_v \rangle_T = \langle n_v \rangle_T / N$ (where $\langle n_v \rangle_T$ is the expected number of vacancies at a fixed temperature T and N the total number of atoms) is between 10^{-3} and 10^{-4} for metals [7], increasing from this point on according to Arrhenius' law:

$$\langle f_v \rangle_T = \exp(-E_v/k_B T) \tag{1}$$

where E_v is the free energy of formation of thermal vacancies [7]. It could be naturally assumed that the underlying probability distribution for this expectation is the normal or Gaussian distribution, and this we believe is an hypothesis worth testing. One implication of a distribution other than a Gaussian, is that the probability of extreme values of concentration of vacancies could be higher.

In this work we provide evidence from atomistic computer simulations supporting a Gamma model for the concentration of thermal vacancies in copper near T_m (but below T_{LS}). The work is organized as follows. Section 2 shows a detailed description of the molecular dynamics and vacancy recognition procedures. Section 3 shows the details of the inference process employed for the statistical comparison of the Gamma and normal models for vacancy distribution. Section 4 comments on the scope and implications of our results.

2. Simulation techniques

We are interested in the formation of thermal vacancies in an isolated and initially perfect crystal (free of intrinsic vacancies and surfaces). As a simple model of the interatomic interactions in

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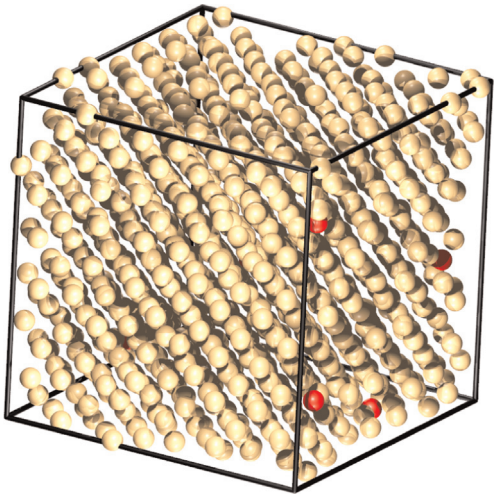

Fig. 1. Copper structure snapshot from the MD simulation at $T=1400$ K. The structure has 1372 atoms, with an initial FCC crystalline structure. The red spheres represent thermal vacancies located with the *Search-and-Fill* algorithm. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

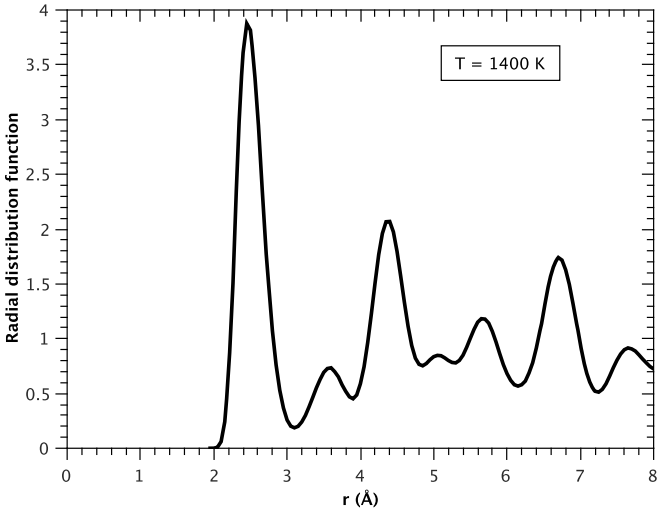

Fig. 2. Pair distribution function for copper at $T=1400$ K. It shows that the structure remains FCC, with the usual broadening of the peaks due to temperature.

such a solid, we consider the embedded atom model of copper, the Sutton–Chen potential, with the usual parameterization [8].

We simulated a face-centered cubic (FCC) copper structure composed of 1372 atoms ($7\times7\times7$ unit cells), with a lattice parameter (corresponding to room pressure) of $a=3.61$ Å, as shown in Fig. 1, in the microcanonical ensemble (i.e., with fixed N, V and E). We used classical molecular dynamics (MD) simulations with periodic boundary conditions at different initial kinetic energies, by means of the LPMD software package [9].

We considered four different initial temperatures T_0, namely 2300, 2500, 2600, and 2700 K, resulting in equilibrium temperatures of $T\sim T_0/2$ in each case, due to the law of equipartition of energy. In each case we simulated a total of 50 ps, with a timestep $\Delta t=1$ fs. This procedure ensures that equilibration is achieved without the use of thermostats which could distort the natural dynamics of the system. This is the same microcanonical approach used in the Z-method [10]. The target equilibrium temperatures, between 1200 K and 1400 K, were chosen in order to be near the experimental melting point of copper, $T_m\sim1360$ K. In this way we have a non-zero probability of observing thermal vacancies given the relatively small size of the system.

We computed the radial distribution function $g(r)$ for all the temperatures in order to check that we indeed have a solid structure in all cases. Fig. 2 shows the $g(r)$ for the case of $T=1400$ K, all the other temperatures being almost identical. In this figure we can see that the nearest-neighbors peak is located around $r=2.5$ Å, which gives the approximate radius of a spherical vacancy to be close to 1.25 Å.

To determine the number of vacancies generated during the simulations, the *Search-and-Fill* algorithm [11] was used. This technique generates virtual spheres in the simulation cell (of radius R_0) and tries to place them with minimum overlap with the atoms. Every site where a virtual sphere can fit with an overlap below a threshold Omega is identified as a vacancy and the site is filled (i.e., the site is not considered empty for the purposes of locating the next vacancy). In the particular case of copper we used the values of $R_0=1.275$ Å and the threshold overlap parameter $\Omega=0.4$.

The average results obtained from the vacancy recognition procedure are presented in Table 1. As expected, the concentration of vacancies increases with temperature.

Table 1
Values of the average concentration of thermal vacancies for several temperatures.

T (K)	$\langle f_v\rangle$ (10^{-3})
1200	2.06195
1300	3.22012
1350	3.97303
1400	4.62318

3. Vacancy distribution

In order to determine the statistical distribution of thermal vacancies we estimated its concentration on each snapshot of atomic positions from the simulation, after equilibration. The vacancy histograms for four different temperatures are displayed in Fig. 3.

We propose two models for the probability distribution of vacancies, a Gaussian distribution:

$$P(f_v|\mu,\sigma)=\frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{1}{2\sigma^2}(f_v-\mu)^2\right) \tag{2}$$

where μ and σ^2 are the mean and variance of f_v, respectively, and a Gamma distribution, given by

$$P(f_v|k,\theta)=\frac{1}{\Gamma(k)\theta^k}f_v^{k-1}\exp(-f_v/\theta) \tag{3}$$

where k and θ are its shape and scale parameters, respectively. In both cases the parameters of the distributions are functions of T. In order to compare both models using data from our simulations for each target temperature, we employed the Bayesian Information Criterion (BIC) [12], defined as

$$\mathrm{BIC}=-2\ln L(\hat{\boldsymbol{\lambda}}_{\mathbf{0}})+n_p\ln N, \tag{4}$$

where $L(\boldsymbol{\lambda})$ is the likelihood function for the model, $\boldsymbol{\lambda}_{\mathbf{0}}$ are the most probable parameters according to the maximum likelihood method, n_p is the number of parameters in the model and N is the number of data points. In this method, the lower the value of BIC, the better (the model gives a better fit to the data). In our case, the second term is the same for both models, and so the comparison