Influence of Point Defects on the Shear Elastic Coefficients and on the Melting Temperature of Copper

Amit Kanigel, Joan Adler and Emil Polturak

Department of Physics, Technion-IIT, Haifa 32000, Israel.

(May 5, 2021)

We present molecular dynamics simulations of the influence of point defects on the shear elastic coefficients of copper. We find that vacancies do not influence these coefficients at all, while the introduction of interstitials causes a large reduction in the elastic coefficients. The simulations establish a phase diagram of the melting temperature as a function of the density of interstitials. A crystal having no free surface undergoes bulk mechanical melting as a result of the vanishing of \( C' \equiv (C_{11} - C_{12})/2 \) once the specific volume reaches a critical value, equal to the experimental volume of liquid phase. This critical volume is history independent, in the sense that it can be reached either by heating the crystal or by adding defects at a constant temperature. These results generalize the Born model of melting for the case where point defects are present.

I. INTRODUCTION

Single phase models of bulk melting usually treat this process as a destabilization of the solid due to proliferation of crystalline defects or excitations. Among these, Lindemann suggested that melting occurs when the amplitude of atomic vibrations exceeds a critical value. Born proposed that melting is connected with the vanishing of the shear elastic coefficients. Other models suggest that melting is a consequence of the proliferation of intrinsic crystalline defects such as vacancies. However, there is no clear experimental evidence supporting any one of these models, all of which rely on a single type of defect or excitation. A model of melting involving interstitials coupled to shear strains proposed by Granato is an exception as it involves coupling of defects and excitations.

Recently, a dramatic decrease of the shear resistance was observed near the bcc-hcp transition of solid \(^4\)He. These observations could have been interpreted as resulting from a coupling of point defects with a phonon which softens near the transition. Were it not for the bcc-hcp transition, one could envisage a continuation of this process until the crystal would melt. Thus, we have experimental evidence of a microscopic process which can potentially lead to melting. However, this scenario requires a coupling of phonons and point defects, and therefore supports a picture similar to Granato’s, in which more than one type of excitation is involved. To understand this further, it is necessary to investigate how point defects couple to phonons, and how this influences the shear resistance. In the following, we report results of molecular dynamics (MD) simulations of the influence of point defects on the elastic properties of copper. Copper was chosen because of the large body of experimental data to which the results of the simulations can be compared. We focus on the shear elastic coefficients, with the intention to test the Born model in the presence of point defects.

II. SIMULATION METHOD

We performed molecular dynamics simulations on samples containing up to 2048 atoms using the “Tight-Binding (TB) Potential” with parameters calculated by Cleri and Rosato appropriate to copper. Newton’s equations were solved using Gear’s Predictor-Corrector algorithm. For temperature control we used the method known as the Nose-Hoover thermostat. The method of Berendsen was used to calculate the volume of the samples. This method does not generate trajectories in the constant NPT (here, \( N \) denotes the constant number of atoms, \( P \) is the constant pressure, and \( T \) is the temperature) ensemble, but it sets the mean value of the pressure to the desired one while predicting the correct volume of the system. For ensemble average calculations we used the Parrinello and Rahman (PR) method. The statistical ensemble created by the Parrinello Rahman combined with Nose’s thermostat was identified as the isothermal-isotension (NtT) ensemble of statistical mechanics. We calculated the elastic constants using a fluctuation formula in both the canonical and in the NtT ensembles.

In the NtT ensemble the formula for the isothermal elastic constants \( C_{ijkl} \) is
\[ \delta(\epsilon_{ij}\epsilon_{kl}) = k_B T C_{ijkl}^{-1}/V_0 \]  

(2.1)

where \( \epsilon \) is the strain and \( V_0 \) is the volume of the sample at zero strain. Calculating elastic constants using this formula involves two steps. First we have to find the reference matrix, \( h_0 \), defining the shape of the simulation box. The condition which determines the shape of the box is that the sample is at zero stress. After running the simulation to calculate \( h_0 \), the program should be used again to calculate the fluctuations. Not many studies have been made using this method because of the very slow convergence of the strain fluctuations.

In the constant NVT ensemble (here, \( N \) denotes the constant number of atoms, \( V \) is the constant volume, and \( T \) is the temperature), MD can determine the elastic constants by using fluctuation formulas derived by Ray and Rahman:

\[ C_{ijkl} = -\frac{V_0}{k_B T} \delta(\sigma_{ij}\sigma_{kl}) + \frac{2N K_B T}{V_0} \delta_{ik}\delta_{jl} + \delta_{im}\delta_{jk} + < B > \]  

(2.2)

where \( \delta_{ij} \) is the Kronecker delta and \( < B > \) is the ensemble average of the Born term, defined as

\[ B = (\partial^2 V / \partial r_{ab}^2 - (\partial V / \partial r_{ab})/r_{ab})r_{abi}r_{ajk}r_{abk}r_{abl} \]  

(2.3)

where \( i,j,k,l \) are the indices of the elastic constants tensor. This formula for calculating the elastic constants is much less compact than the NtT formula, mainly because it contains the explicit second derivative of the inter atomic potential. The main advantage of this method, and the reason for it being used more than the NtT method, is the faster convergence of the stress-stress fluctuation term relative to the convergence of the strain-strain fluctuation term. Two steps are required to calculate the elastic constants using this formula. As in the NtT formalism first one has to find the zero stress reference matrix and volume \( h_0 \) and \( V_0 \) and then run the NVT MD program to calculate the elastic constants using equation (2.2).

### III. VALIDATION AND COMPARISON WITH EXPERIMENT

In order to validate the programs and to check the potential at various conditions we performed a series of calculations of the physical properties of copper using our programs and compared the results with experimental data.

First, we calculated the thermal expansion up to the melting point at zero external pressure. Our results are compared with neutron scattering data in Fig. 1. As expected, the calculated values are close to the experimental values at low temperatures (We must bear in mind that the lattice constant at zero temperature was used as input in the fitting of the potential). The agreement remains good even at elevated temperatures, with a maximal difference of about 10%.

Secondly, the phonon spectrum, \( \omega(\vec{k}) \), was determined by calculating the time Fourier-transform of the following quantities:

\[ f_{\alpha}(\vec{k}, t) = \sum_{i=1}^{N} (\vec{u}_\alpha \cdot \vec{v}_i) \cos(\vec{k} \cdot \vec{r}_i) \]  

(3.1)

where, \( \vec{r}_i \) and \( \vec{v}_i \) are the time dependent positions and velocities of the \( i \)th atom. The polarization vectors are defined as \( \vec{u}_l = \vec{k}/k \) in the longitudinal case, while \( \vec{u}_{11} \) and \( \vec{u}_{12} \), the transverse polarizations, are perpendicular to \( \vec{u}_l \) and to each other.

We then calculated the phonon spectrum along the (100) and (110) directions. Due to the importance of long-time correlations the calculations were made under conditions of constant energy without temperature control. We ran the MD program for 20000 time steps with temperature and pressure control, 10000 time steps with temperature control only, and then \( f_{\alpha}(\vec{k}, t) \) was saved to disk during 200000 time steps under energy conservation conditions. The resulting spectrum, shown in Fig. 2, is in good agreement with neutron scattering data.

Thirdly, to test the algorithms used to obtain the elastic constants, we calculated their variation with temperature using both approaches described in section II. The system was initially equilibrated for 50000 steps, and 300000 subsequent steps were used to calculate the fluctuations. We found that the convergence of the PR method was slower than that of the NVT method. To monitor the convergence of the algorithm, we compared values of the elastic coefficients calculated along directions which are symmetrically equivalent. In the final result, after 300000 time steps, in both methods, the three equivalent elastic constants differ by no more than 10%. From this variance, one can estimate the accuracy of the calculation. Comparison with the experimental values measured by neutron scattering shows that the shear moduli of the model-lattice and of real copper soften in the same way within the estimated accuracy of the simulations (e.g. 10%). The results are shown in Fig. 3.

The typical computer time needed to calculate the elastic constants varies between 4 days for a calculation in the NVT ensemble to one week in the NtT ensemble on a Pentium-Pro computer.
IV. INFLUENCE OF POINT DEFECTS

After successful validation of the pure system, point defects were introduced into the lattice by either removing an atom (vacancy) or adding one (interstitial). The simulations were done using a box having a fixed number of sites. Periodic boundary conditions were used throughout. In order to prevent mutual annihilation of the defects, we used defects of only one species in each run. We first used simulated annealing to find the most stable configuration of a vacancy and of an interstitial in the model. The formation energy of a vacancy was found to be 1.27eV. The lowest energy configuration of an interstitial atom was found to be a (110)-split interstitial with a formation energy of 3.28eV. These formation energies agree well with experimental data and with previous simulations. Formation energies of other possible configurations of interstitials were determined using the conjugate gradient method, and are summarized in Table I. We point out that the difference between these energies is on the order of 0.1 eV (∼1000K), which means that interstitials of various configurations may be present at high temperatures.

The influence of point defects was determined by calculating the shear elastic coefficients in samples containing different concentration of defects using MD. For any concentration of defects, the number of atoms and unit cells in the sample is kept constant, so that the number of externally introduced defects is conserved. Under this constraint, atoms and defects are free to diffuse, agglomerate etc. We first discuss vacancies. We found that the influence of vacancies on the shear elastic coefficients is too small to be resolved within our stated accuracy. For example Fig. 4 shows that $C_{44}$ is independent of the concentration of vacancies. This is correct both at low temperatures and near the melting point. Previously, influence of vacancies on the elastic properties at zero temperature was treated analytically by Dederichs et al., who also reviewed earlier work. The two body potentials used by these authors are less accurate than the one used here. They found a reduction of 2-3 % in the values of $C_{44}$ and 1.5-3 % in values of $C'$ per percent of vacancies. The effect is indeed small, falling within the uncertainty limits of our calculation.

We turn now to the influence of interstitials. In contrast to the vacancies, interstitials seem to cause a large softening of the shear moduli. We turn to the influence of interstitials. In contrast to the vacancies, interstitials seem to cause a large softening of the shear moduli. (see Fig. 3). At low temperatures, we can qualitatively compare the results with the analytical calculation of Dederichs et al., made at T=0K, and with the irradiation experiment of Holder et al., made at T=4.2K In the latter, the defects produced by the irradiation are Frenkel pairs and not interstitials. The common trend is that defects induce a large softening of the shear moduli. The softening is anisotropic, meaning that $C_{44}$ softens more than $C'$. Bearing in mind the different conditions under which the different studies were made, the qualitative agreement can be regarded as good.

The main new thrust of this work regards studying the influence of point defects on the shear moduli at increasingly higher temperatures, up to the melting temperature $T_M$. We emphasize that due to the use of periodic boundary conditions, the crystal can be super-heated and $T_M$ is higher than the thermodynamic melting temperature.

In general, our results can be explained by the combined effect of volume change and the dia-elastic effect. Volume changes resulting from introduction of defects arise due to the specific volume per defect being larger than that of an atom residing at a normal lattice site. We can compare the change of the elastic coefficients caused by defects with that induced by heating the crystal up to a temperature where thermal expansion increases the volume by the same amount. If the dependence of the elastic coefficients on the volume is the same, it would mean that effect of the defects is simply to expand the lattice. We demonstrate such a comparison in Fig. 5 for data obtained at T=400K. As one can see in this figure, the change of $C'$ due to thermal expansion (without defects) is identical with that induced by increasing density of defects at a constant temperature when plotted against the lattice constant. This proves that $C'$ is affected only by volume changes. On the other hand, the change of $C_{44}$ due to thermal expansion is very different from that induced by increasing the density of defects, and cannot be explained by the volume increase alone. We attribute this behavior to the dia-elastic effect. Briefly, the dia-elastic effect describes the coupling of the internal vibration modes of the interstitial with the phonons. Some of the internal vibration modes, the so called resonance modes, have frequencies within the band of the usual lattice spectrum. Mode coupling will lower the long wavelength part of the phonon branch related to the elastic coefficients. For example, the (100) split interstitial is coupled to (100) shear strain. If the lattice is deformed in this way the response of the atoms forming the defect would be larger than the response of atoms occupying normal lattice sites. The large response leads to a reduction of $C_{44}$ elastic coefficient. On the other hand, $C'$ is associated with (110) shear strain, which does not couple to the (100) split interstitial. Consequently, the decrease of $C'$ is induced only by volume expansion, as indeed seen in Fig 5.

Our results indicate that at high temperatures we can make one of the shear moduli vanish by adding a sufficient number of self-interstitials to the sample. The number of defects needed for this purpose is temperature dependent. The absolute change of the shear moduli per % of interstitials is larger for $C_{44}$ at all temperatures, as summarized in Table II.

However, the relative sensitivity of $C'$ becomes larger at high temperatures as melting is approached. Because its initial value at elevated temperatures is already very small. This is plotted in Fig. 6. Consequently, $C'$ is the first one to vanish. This result is quite surprising, as it is opposite to what one would expect based on the low temperature
We determined the melting temperature within our model at different temperatures and defect concentration, by monitoring the structural order parameter after 200000 time steps. The results are summarized in Fig. 7. Each point in the figure represents the results of several runs made at constant T and with the same defect density, but at a different random initial configuration. The melting process found is mechanical melting, and the sample collapses due to the vanishing of $C'$. This was found by correlating the temperatures at which $C'$ vanishes with the melting temperature. The melting process is rather fast, its duration being on the order of a typical vibration time of the crystal. Thus, this is a bulk melting mechanism. As can be seen from our results the interstitials reduce the mechanical melting point, and a concentration of about 0.005 lowered the melting point by about 60°K. The same cannot be said about vacancies, which did not reduce the mechanical melting point even at very high concentration (up to 4%).

It turns out that the specific volume per atom at the phase boundary in Fig. 7 is fixed at 13.31 Å$^3$. The same specific volume is found by extrapolating the dependence of $C'$ on the volume to the value at which $C'=0$. This specific value is consistent with the specific volume of the liquid phase at T=1356K, the thermodynamic melting temperature, as suggested previously. The way one reaches that specific volume, either by heating or by adding defects at a constant temperature does not seem to matter.

In summary, we have simulated the influence of point defects on the shear moduli of Cu at temperatures up to $T_m$. Mechanical melting occurs due to the fulfillment of the Born criterion, where one of the shear moduli of the solid vanishes. We found that mechanical melting of the crystal is brought about by the vanishing of $C'$, rather than that of $C_{44}$. Melting occurs once the specific volume reaches a critical value. This value is independent of the path by which it is reached, either by thermal expansion alone, or by any combination of thermal expansion and of expansion due to interstitials introduced into the sample. Since the specific volume per vacancy is smaller than the atomic volume, vacancies do not expand the crystal. Hence, vacancies play no role in bulk melting.

V. ACKNOWLEDGEMENTS

We are grateful to David Saada, Adham Hashibon, Zaher Salman for their contribution to this project, and IUCC for the use of the computer facilities. We thank R. W. Cahn for his comments. This work was supported in part by the Israel Science Foundation and by the VPR Technion Fund for the Promotion of Research.

| Configuration   | $E_f$ (eV) |
|-----------------|------------|
| vacancy         | 1.27       |
| (100) split     | 3.28       |
| Octahedral      | 3.45       |
| (110) split     | 3.55       |
| (111) split     | 3.78       |

TABLE I. Formation energies of various point defects.

| Temp(K) | $\Delta C_{44}(\text{GPa/}%\text{inters.})$ | $\Delta C(\text{GPa/}%\text{inters.})$ |
|---------|----------------------------------------|--------------------------------------|
| 400     | $-39 \pm 13$                           | $-4.5 \pm 2.5$                       |
| 1400    | $-23 \pm 1.7$                          | $-3.5 \pm 2.0$                       |
| 1450    | $-18 \pm 2.5$                          | $-4.1 \pm 2.0$                       |
| 1480    | $-15.5 \pm 1.3$                        | $-7.8 \pm 3.5$                       |

TABLE II. Change in shear moduli per percent of self-interstitials at various temperatures.
FIG. 1. Thermal expansion coefficient of copper as a function of temperature obtained from our simulations compared with data determined by a neutron scattering experiment\(^\text{16}\).

FIG. 2. Phonon dispersion curve at 400K along (100) and (110). Solid lines are the result of the simulations, while the circles are experimental results at 80K\(^\text{18}\).
FIG. 3. Variation of the shear moduli with temperature: PR method, •; NVT MD, ◦; experimental data, dashed line.

FIG. 4. Dependence of $C_{44}$ on the concentration of defects at $T = 1400\,K$, showing the difference between the influence of vacancies and interstitials.

FIG. 5. The variation of the shear moduli vs. the lattice constant. The solid line represents thermal dilation and the symbols represent dilation due to interstitials. The dashed line is a guide to the eye.
FIG. 6. Relative softening of the shear moduli per percent of interstitials as function of temperature. The lines are guides to the eye.

FIG. 7. The influence of self interstitials on the melting temperature obtained using periodic boundary conditions (a crystal without free surfaces).

1 Ubbelohde A.R., *Melting and Crystal Structure*, Clarendon Press, Oxford 1965.
2 Born M., J. Chem. Phys., 7, 591 (1939).
3 Frenkel D., *Kinetic Theory of Liquids*, Dover Publications, Inc. New-York 1955.
4 Granato A.V., Phys. Rev. Lett., 68, 974 (1992); Granato A.V., Metallurgical and Materials Trans. 29A, 1837 (1998).
5 Berent I. and Polturak E., Phys. Rev. Lett., 81, 846 (1998).
6 Ducastelle F., *Computer Simulations in Materials Science*, edited by M. Meyer and V. Pontikis, Kluwer, Dordrecht, 1991.
7 Cleri F. and Rosato V., Phys. Rev., B48, 22 (1993).
8 Allen M. P. and Tildesley D. J., *Computer Simulation Of Liquids*, Clarendon Press, Oxford, 1987.
9 Hoover W.G., Phys. Rev., A31, 1695 (1985).
10 Berendsen H.J.C., Postma P.M., van Gunsteren W.F., DiNola A. and Haak J.R., J. Chem. Phys, 81, 3684 (1984).
11 Parrinello M. and Rahman A., Phys. Rev. Lett., 45, 1196 (1980).
12 Ray J.R. and Rahman A., J. Chem. Phys., 80, 4423 (1984).
13 Ray J.R. and Rahman A., J. Chem. Phys., 82, 4243 (1985).
14 Ray J.R., Comp. Phys. Repts., 8, 109 (1988).
15 Wolf R.J., Mansour K. A., Lee M. W., and Ray J. R., Phys. Rev., B46, 8027 (1992).
16 Larose A and Brockhouse B. N., Can. Jour. Phys., 54, 1990 (1976).
Caprion D., Jund P., Jullien R., Phys. Rev. Lett., 77, 675 (1996).
Nilsson G., and Rolandson S., Phys. Rev, B7, 2393 (1973).
Amihai Silverman and Joan Adler, Computers in Physics, 6, 277 (1992).
Wollenberger J.J., Physical Metallurgy, edited by Cahn R.W. and Haasen P., North-Holland, Amsterdam 1983.
Dederichs P.H., Lehmann C. and Scholz A., Z. Physik, B20, 155 (1975).
Holder J., Granato A. V., and Rehn L. E., Phys. Rev., B10, 349, (1974), ibid., 363 (1974).
Dienes G.J., Phys. Rev., 86, 228 (1952).
Dederichs P.H., Lehmann C., Schober H.R., Scholz A. and Zeller R., J. of Nuclear Mat., 69 & 70, 176 (1978).
Dederichs P.H., Lehmann C. and Scholz A. Phys. Rev. Lett., 31, 1130 (1973).
Wolf D., Okamoto P. R., Yip S., Lutsko J. F., and Kluge M., Jour. Mat. Res., 5, 286 (1990).
Tallon J. L., Phil. Mag., A39, 151 (1979).