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Using modified potential to account for non-zero temperature in molecular statics for crystals

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Abstract

A modified interatomic potential, which allows taking into account the thermal expansion of the bonding distance at the non-zero temperature and thus the application of the molecular statics to study the effect of temperature on fracture in crystals, is suggested. The approach is demonstrated on a 2D imperfect crystal in which the interatomic pair-wise forces are governed by the Lennard–Jones type potential. A comparison of stress–strain curves, dislocation formation and fracture, and transformation of interatomic forces is made for a crystal with deficiency at zero and non-zero temperatures.

Keywords: Crystals; Modified potential; Molecular statics; Simulation

1. Introduction

The fundamental assumption of molecular statics is that at 0 K the atoms positions are fixed, i.e. their kinetic energy is zero, and thus the equilibrium of the atomic system is defined by the minimum of its potential function. At the non-zero temperature the atoms oscillate, and the higher the temperature the larger the amplitudes of these oscillations. Since repulsive forces between the atoms are stronger than the attractive ones, the average positions of atoms are displaced with relative to those at the zero temperature. This displacement of the average atomic positions results in an increase of the macroscopic size of a material specimen and it defines its thermal expansion. The asymmetry of the phenomenological interatomic bond-energy curve reflects this thermal expansion [1,2]. In molecular dynamics it is assumed that interatomic potentials are the same as at 0 K while the kinetic energy due to atoms oscillations takes into account the non-zero temperature. Thus the potential is temperature independent. An approach when the temperature-dependence of the potential is taken into account was explored within the molecular dynamics formulation [3]. In the latter paper, the atoms positions are not fixed at the 0 K but are temperature-dependent and thus “one can use a molecular statics relaxation code to study thermodynamic properties of defects” by using modified interatomic potentials.

In this paper, we assume that the thermal expansion of the lattice is known and it is defined by the asymmetry of the interatomic bond-energy curve at 0 K. This leads to modified interatomic potentials with equilibrium of atomic positions corresponding to the non-zero temperature and thus to the application of molecular statics methods. The approach is demonstrated on a 2D imperfect crystal in which the interatomic pair-wise forces are governed by the Lennard–Jones (LJ) type potential. A static analog of molecular dynamics suggested in [4] is applied to simulate the tensile loading of the crystal at zero and non-zero temperatures. The resulting stress–strain curves, the phenomenon of dislocation formation, and the transformation of interatomic forces are compared at both temperatures.

2. Defining the non-zero temperature quasi-potentials

In the following the LJ pair-wise interaction potentials between the atoms are used in a normalized form

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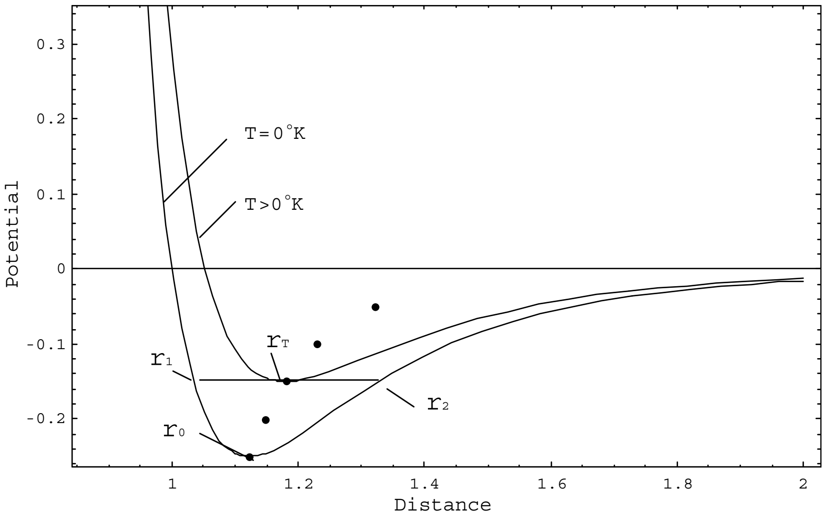

Fig. 1. A schematic representation of the LJ potential at two temperatures and the positions of interatomic equilibrium distances (dots).

$$\beta(T)\phi_0(r_{ij}) = a(T)r_{ij}^{-12} - b(T)r_{ij}^{-6}, \tag{1}$$

where $\phi_0(r_{ij}) = \frac{\Phi_0(r_{ij})}{4\varepsilon}, r_{ij} = \frac{R_{ij}}{\sigma}, \Phi_0(r_{ij})$ is the binding energy at 0 K and R_{ij} is the distance between the atoms i and j, ε defines the strength of the interaction, σ is the distance scaling factor, $0 < r_{ij} \leqslant r_c$, where r_c is a cut-off distance, and $\beta(T)$, $a(T)$, $b(T)$ are the temperature-dependent parameters. At $T = 0$ K, $\beta(T) = 1$, $a(T) = 1$ and $b(T) = 1$.

For any $T > 0$ K there is a $\beta(T) < 1$, which corresponds to a reduced binding energy at any interatomic distance. A constant $\beta(T)\phi(r_0)$, where r_0 is the equilibrium distance between the atoms at 0 K, defines a line intersecting the zero temperature potential at the points r_1 and r_2 in Fig. 1. The middle point r_T defines the equilibrium position of oscillating atoms at elevated temperature. This middle point is used to define a modified potential by formulating two requirements. Namely, that at $r = r_T$, $\phi(r_T) = \beta(T)\phi(r_0)$ and $\frac{\mathrm{d}\phi(r)}{\mathrm{d}r} = 0$. From these two requirements the two parameters, $a(T)$ and $b(T)$, are found for a given $\beta(T)$. The corresponding two equations are

$$a(T)r_T^{-12} - b(T)r_T^{-6} = \beta(T)\phi_0(r_0), \tag{2}$$

$$-12a(T)r_T^{-13} + 6b(T)r_T^{-7} = 0, \tag{3}$$

where $\phi(r_0) = -0.25$ for the LJ potential.

The distance $\Delta r = r_T - r_0$ is determined by the temperature increment ΔK and the coefficient of thermal expansion α. Assuming that the latter is known, then from the definition of it

$$\alpha = \frac{\Delta r}{r_0 \Delta K} \tag{4}$$

and the expression for r_T

$$r_T = 0.5(r_1 + r_2) \tag{5}$$

for any ΔK the coefficient $\beta(T)$ an be found since points r_1 and r_2 are β-dependent. Indeed, the equation defining these roots is

$$r_{ij}^{-12} - r_{ij}^{-6} = \beta(T)\phi_0(r_0) \tag{6}$$

and the corresponding roots are

$$r_1 = \left(0.5 + \sqrt{0.25 + \beta(T)\phi_0}\right)^{-1/6} \tag{7}$$

and

$$r_2 = \left(0.5 - \sqrt{0.25 + \beta(T)\phi_0}\right)^{-1/6}. \tag{8}$$

From Eq. (4) the equation for the coefficient $\beta(T)$ follows:

$$0.5(r_1 + r_2) = r_0(1 + \alpha\Delta K). \tag{9}$$

To summarise, the algorithm for constructing a modified potential is as follows:

1. From Eq. (9) find the coefficient $\beta(T)$ for any temperature increment ΔK.
2. From Eqs. (5), (7) and (8) find the interatomic distance r_T.
3. From Eqs. (2) and (3) find the coefficients $a(T)$ and $b(T)$. defining the potential according to Eq. (1)

As soon as the modified potential function is defined, any molecular statics method can be applied to find the system equilibrium. In the following, an iterative process for finding the state of equilibrium by moving each atom independently in such a way that the resultant forces converge to a prescribed minimum developed in [4] is used. The normalized interatomic forces follow from Eq. (1) and are equal to

$$f(r_{ij}) = -12a(T)r_{ij}^{-13} + 6b(T)r_{ij}^{-7}. \tag{10}$$

3. Results

The numerical results were obtained for a 2D crystal structure by simulating the extension of a basal plane of