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An extension of the quasicontinuum treatment of multiscale solid systems to nonzero temperature

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Covering the solid lattice with a finite-element mesh produces a coarse-grained system of mesh nodes as pseudoatoms interacting through an effective potential energy that depends implicitly on the thermodynamic state. Use of the pseudoatomic Hamiltonian in a Monte Carlo simulation of the two-dimensional Lennard-Jones crystal yields equilibrium thermomechanical properties (e.g., isotropic stress) in excellent agreement with "exact" fully atomistic results. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1806811]

I. INTRODUCTION

The behavior of microscopic defects in solids generally involves large-amplitude (diffusive) atomic motions in the vicinity of the defect ("near" region) coupled with small-amplitude atomic displacements in "far" regions (i.e., regions of the solid far removed from the defect). To achieve a reliable quantitative description of crack propagation, for example, one is obliged to treat the near region at the atomic scale, that is to track individual atoms. On the other hand, it is sufficient to handle the far region at the continuum scale. Based on this notion, a variety of multiscale treatments that merge atomistic and continuum descriptions have been proposed since the early 1990's.[1–10]

Of particular interest here is the quasicontinuum (QC) technique of Tadmor *et al.*,[3] in which the atomic lattice is coarse grained by overlaying it with a finite-element mesh. Thereby, most atoms are explicitly eliminated; only the nodes remain as pseudoatoms. The static configuration of the nodes is determined at zero temperature ($T=0$ K) by minimizing the potential (configurational) energy under prescribed boundary conditions. By varying the boundary conditions incrementally, one can trace the quasistatic evolution of (metastable) defects.

In a previous article,[11] we proposed an extension of the QC method to treat solid systems at nonzero temperature. The idea is to introduce thermal effects by requiring nodal configurations in phase space to satisfy Boltzmann's distribution. Thermomechanical properties are then given as ensemble averages, which are effected, in practice, by means of Monte Carlo (MC) computer simulation. We applied this extended QC technique to a pure single two-dimensional (2D) crystal of Lennard-Jonesium, comparing the "coarse-grained" isotropic stress τ_c (i.e., the isotropic stress computed using the pseudoatomic Hamiltonian) with the "atomistic" stress τ (i.e., the stress computed using the original atomic Hamiltonian), which is taken to be "exact." The absolute error in the coarse-grained stress, $\Delta\tau=\tau-\tau_c$, which is proportional to $N-N_n$, the difference between the total number of atoms and the number of nodes (i.e., the number of non-nodal atoms that lie under the finite-element mesh), is due to neglect of thermal motions of the underlying (non-nodal) atoms. Their random thermal oscillations are quenched through the dynamical constraint that they move in lockstep with the nodes.

The purpose of the present article is to propose an alternative extension of the QC technique, which avoids the dynamical constraint on underlying (non-nodal) atoms. By integrating over the phase space of the underlying subsystem in the classical canonical partition function, we obtain an effective potential energy V_{eff} for the nodal motion that depends on the thermodynamic state of the underlying subsystem. That is, V_{eff} consists of the potential energy of the dynamically constrained system plus the Helmholtz potential of the subsystem in the field of the nodal atoms fixed in the given configuration. The free-energy term accounts precisely for the thermal motion of the underlying atoms that is neglected in the original dynamically constrained treatment.[11] We tested the proposed new extension of the QC, method on the 2D Lennard-Jones crystal, for which we have data from fully atomistic simulations.[11]

II. MODEL AND COARSE GRAINING

Figure 1 displays a schematic of the reference configuration at $T=0$ K. The system is bounded by the L_xXL_y rectangle, which encloses 2^{2p+1} unit cells, each of which contains just one atom. Periodic boundary conditions (PBC) are enforced in the x and y directions. Only isotropic deformations of the lattice are allowed. Hence, the dimensions of the system are expressible in terms of the lattice constant a as $L_x=a(N/2)^{1/2}$ and $L_y=\sqrt{3}L_x$. The density is given by $\rho=2/(\sqrt{3}a^2)$. The thermodynamic state is specified by the absolute temperature (T), the number of atoms (N), and the area ($A=L_xL_y$). Reversible transformations are governed by Gibbs' fundamental relation

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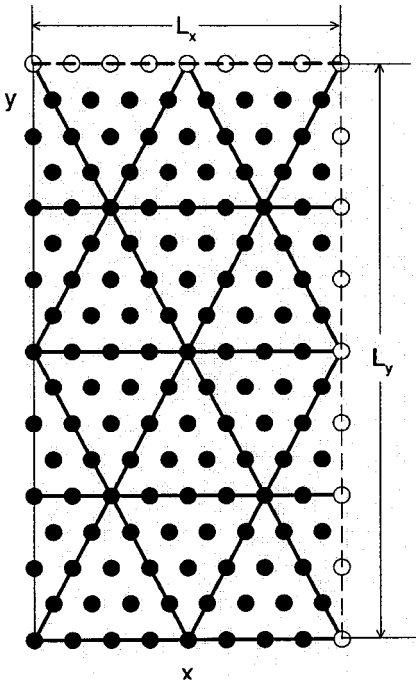

FIG. 1. Schematic of the two-dimensional Lennard-Jones crystal.

$$dF = -SdT + \mu dN + \tau dA,$$

where F denotes the Helmholtz energy S the entropy μ the chemical potential and τ the isotropic stress. The bridge between the macroscopic and microscopic scales is provided by the relation

$$F = -k_B T \ln Q,$$

where $Q = Q(N,A,T)$ is the canonical partition function and k_B is the Boltzmann's constant.

The lattice in the reference configuration is coarse grained by means of a finite-element mesh, comprising $N_e = 2^{2q}$ $(q=2,3,...)$ strictly congruent equilateral triangles. There are a total of $N_n = 2^{2q-1}$ independent nodes, when the PBC are accounted for. Underlying each element are $N_a^e = 2^{2(p-q)+1}$ atoms. Figure 1 depicts the special case $p=3$ and $q=2$.

III. EFFECTIVE POTENTIAL ENERGY

Coarse-graining partitions the original atoms into two subsets: N_n primary or nodal atoms and N_s secondary or non-nodal atoms. By formally carrying out the integrals over the secondary phase space (and primary momentum space) in the classical canonical partition function, we obtain

$$Q = \Lambda^{-2N_n} \int dR^{N_n} \exp[-V_{\text{eff}}(R^{N_n})/k_B T],$$

where R^{N_n} stands for the collection of nodal positions, $\Lambda = (h^2/2\pi m k_B T)^{1/2}$ for the thermal de Broglie wavelength, m for the atomic mass, and h for Planck's constant. The effective potential energy can be expressed as

$$V_{\text{eff}}(R^{N_n}) = U(R^{N_n},0) + F_s(R^{N_n}), \tag{1}$$

where $U(r^{N_n},0)$ is the original potential energy with the secondary atoms in their equilibrium configuration (0) (i.e., where the net force on every secondary atom vanishes) in the field of the primary atoms fixed in the configuration R^{N_n}. In Eq. (1),

$$F_s(R^{N_n}) = -k_B T \ln\left[\Lambda^{-2N_s} \int dr^{N_s} \exp(-\Delta U/k_B T)\right]$$

represents the Helmholtz energy of the secondary subsystem in which the atoms are subject to the shifted potential energy, $\Delta U \equiv U(R^{N_n},r^{N_s}) - U(R^{N_n},0)$, where r^{N_s} stands for the collection of secondary atomic positions.

We assume that when a coarse-graining element is distorted by displacing its nodes, the lattice of equilibrium positions (0) of the underlying secondary atoms is homogeneously deformed. In the case of the centrosymmetric lattice under study, this assumption is valid, although it will not generally be so. We also assume that the elements are local,[3] that is, they are sufficiently large that the error committed in neglecting nonuniformities in the number and energy densities near the boundaries of an element is insignificant. We can then write for the potential-energy and secondary free-energy contributions to the effective potential energy

$$U(R^{N_n},0) = \sum_{e=1}^{N_e} N_a^e u_e,$$
$$F_s(R^{N_n}) = \sum_{e=1}^{N_e} N_s^e f_e, \tag{2}$$

where the sums run over all elements and N_s^e is the number of secondary atoms under e. (For the case shown in Fig. 1, $N_s^e = 15/2$.) In Eq. (2), u_e and f_e, respectively, represent the potential energy per atom and the (shifted) Helmholtz energy per atom for an infinite perfect crystal deformed from the given reference configuration according to the displacements of the nodes.

For Lennard-Jonesium, by definition $U = 1/2\Sigma_{i=1}^N \Sigma_{j\neq 1}^N \phi(r_{ij})$, where $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, and r_{ij} is the distance between a pair of atoms. The potential energy per atom is then given approximately by

$$u_e = \tfrac{1}{2}\sum_{j\neq i} \phi(r_{ij}), \tag{3}$$

where the sum on j runs over all atoms that lie within a cutoff circle (centered on reference atom i) at the sites of a lattice deformed according to the displacements of the nodes of element e. To estimate f_e, we utilize the local harmonic approximation,[12] which we have previously shown to be reliable in this context.[11] For the 2D Lennard-Jones crystal

$$f_e = 2k_B T \ln[h(\det D_e)^{1/4}/k_B T], \tag{4}$$

where the elements of the 2×2 dynamical matrix are given by $(D_e)_{kl} = m^{-1}(\partial^2 U/\partial x_k \partial x_l)_0$ $(k,l=1,2)$, k and l label Cartesian components $(x_1 = x,\ x_2 = y)$ of the position of the reference atom, and the subscript 0 signifies that the partial derivative is evaluated at the equilibrium configuration. Note

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TABLE I. Isotropic stress τ^* [Eq. (5)] for 2D Lennard-Jonesium in various solid states (ρ,T) computed by MC simulation of coarse-grained system using V_{eff} [Eq. (1)]. The number in parentheses is coarse-grained stress τ_c based on effective potential $U(R^{Nn},0)$ (see discussion in text). The last column lists the exact stress τ computed by usual fully-atomistic simulation.

ρ	T	$N_n=8$	32	128	Atomistic
0.9	0.001	1.78(1.79)	1.78(1.79)	1.78(1.79)	1.78
	0.010	1.70(1.79)	1.70(1.79)	1.70(1.79)	1.70
	0.100	0.85(1.79)	0.85(1.78)	0.85(1.73)	0.90
	0.200	−0.09(1.79)	−0.09(1.76)	−0.10(1.67)	0.07
1.0	0.001	−5.58(−5.57)	−5.58(−5.57)	−5.58(−5.57)	−5.58
	0.010	−5.66(−5.57)	−5.66(−5.57)	−5.66(−5.58)	−5.66
	0.100	−6.46(−5.57)	−6.46(−5.58)	−6.42(−5.63)	−6.46
	0.200	−7.35(−5.57)	−7.35(−5.60)	−7.35(−5.68)	−7.29
1.1	0.001	−22.97(−22.96)	−22.97(−22.96)	−22.97(−22.96)	−22.97
	0.010	−23.05(−22.96)	−23.05(−22.96)	−23.05(−22.97)	−23.05
	0.100	−23.87(−22.96)	−23.87(−22.97)	−23.87(−23.02)	−23.85
	0.200	−24.77(−22.97)	−24.77(−22.99)	−24.77(−23.07)	−24.73

that D_e is an implicit function of the nodal configuration R^{N_n}, which determines the strain to which the lattice underlying e is subject.

IV. RESULTS AND DISCUSSION

The thermomechanical quantity of principal interest, the isotropic stress, is given by

$$\begin{aligned}\tau &= (\partial F/\partial A)_{N,T} \\ &= -N_n k_B T/A + \left\langle \sum_{k=1}^{N_n} \nabla_{R_k} U(R^{N_n},0)\cdot R_k \right\rangle \Big/ 2A \\ &\quad + \left\langle \sum_{k=1}^{N_n} \nabla_{R_k} F_s(R^{N_n})\cdot R_k \right\rangle \Big/ 2A, \end{aligned} \tag{5}$$

where the angular brackets denote the ensemble average. The first two terms in Eq. (5) arise from the random thermal motion of only the primary atoms (nodes) with the (equilibrium positions of the) secondary atoms constrained to move in unison with them. Following the derivation given in Ref. 11, one can show that this dynamically constrained contribution to the stress agrees approximately with the quantity that was there called simply the coarse-grained stress τ_c. The third term in Eq. (5) accounts for the thermal motions of secondary atoms.

Utilizing the effective potential energy given by the combination of Eqs. (1)–(4), we performed canonical-ensemble Monte Carlo simulations of the coarse-grained system according to the recipe given in Ref. 11. We fixed the total number of atoms ($p=5$, $N=2048$) and computed the isotropic stress τ^* as a function of the degree of coarse graining ($N_n=2^{2q-1}$, $q=2$, 3, 4) for a selection of thermodynamic states (ρ,T). (Note that we symbolize the approximate value of the stress computed from Eq. (5) by τ^* in order to distinguish it from the exact value τ and the dynamically constrained value τ_c.) The results are listed in Table I in the customary units based on the Lennard-Jones interatomic potential: distance in units of σ; energy in units of ϵ; stress in units of ϵ/σ^2; mass in units of the atomic mass m; time in units of $(m\sigma^2/\epsilon)^{1/2}$; and temperature in units of ϵ/k_B. Also included in Table I are coarse-grained (τ_c) and atomistic (exact τ) results.

What stands out immediately from Table I is the excellent overall agreement between τ^* and the exact τ, regardless of the degree of coarse graining. Except for the low-density ($\rho=0.9$), higher-temperature ($T=0.1,0.2$) states, where the solid is under tension ($\tau>0$) and the harmonic approximation might be expected to fail, the difference between τ^* and τ is less than 1%. A close inspection of the numbers indicates that the (absolute) difference between τ^* and τ tends to increase with increasing temperature. This is expected, since as the amplitude of thermal motion increases, anharmonic regions of the true potential contribute to the exact atomistic ensemble average.

In sharp contrast to τ^*, the coarse-grained stress τ_c is in poor agreement with the exact value for all but the lowest-temperature states and does not improve significantly with increasing N_n over the range shown in Table I. Although τ^* varies only slightly (less than 1% for most states) with increasing N_n, its agreement with the atomistic value does not necessarily improve. Nevertheless, even for small N_n, τ^* is sufficiently accurate that one should be able to employ relatively large local elements and expect to account reliably for thermal effects due to secondary atoms. This would be especially advantageous in the context of our hybrid atomistic-coarse-grained multiscale treatment in which only the far regions are coarse grained, and it is necessary to couple ''real'' atoms in the near region with nodes in the far region.[13]

The present extension of the QC technique bears a close resemblance to one proposed by Shenoy *et al.*[14] They introduce random thermal motions in the ''slave'' (secondary) atoms by adding ''fluctuational variables'' to the constrained positions. This leads to an ''effective energy function'' of the same form as V_{eff}. Although differences in terminology and notation make direct comparison difficult, the two methods appear to be equivalent.

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[1] S. Kohlhoff, P. Gumbsch, and H. F. Fischmeister, Philos. Mag. A **64**, 851 (1991).
[2] P. Gumbsch and G. E. Beltz, Modell. Simul. Mater. Sci. Eng. **3**, 597 (1995).
[3] E. B. Tadmor, M. Ortiz, and R. Phillips, Philos. Mag. A **73**, 1529 (1996).
[4] H. Rafii-Tabar, L. Hua, and M. Cross, J. Phys.: Condens. Matter **10**, 2375 (1998).
[5] F. F. Abraham, J. Q. Broughton, N. Bernstein, and E. Kaxiras, Europhys. Lett. **44**, 783 (1998).
[6] R. E. Rudd and J. Q. Broughton, Phys. Rev. B **58**, R5893 (1998).
[7] R. E. Rudd and J. Q. Broughton, Phys. Status Solidi B **217**, 251 (2000).
[8] R. Phillips, M. Dittrich, and K. Schulten, Ann. Rev. Mater. Res. **32**, 219 (2002).
[9] R. E. Miller and E. B. Tadmor, J. Comput.-Aided Mater. Des. **9**, 203 (2002).
[10] R. E. Miller, Int. J. Multiscale Comput. Eng. **1**, 57 (2003).
[11] Z.-B. Wu, D. J. Diestler, R. Feng, and X. C. Zeng, J. Chem. Phys. **119**, 8013 (2003).
[12] J. Rickman and R. LeSar, Ann. Rev. Mater. Res. **32**, 195 (2002).
[13] Z.-B. Wu, D. J. Diestler, R. Feng, and X. C. Zeng, J. Chem. Phys. **120**, 6744 (2004).
[14] V. Shenoy, V. Shenoy, and R. Phillips, Mater. Res. Soc. Symp. Proc. **538**, 465 (1999).

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