Dynamics of an Inhomogeneously Coarse Grained Multiscale System

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To study material phenomena simultaneously at various length scales, descriptions in which matter can be coarse grained to arbitrary levels are necessary. Attempts to do this in the static regime (i.e., zero temperature) have already been developed. We present an approach that leads to a dynamics for such coarse grained models. This allows us to obtain temperature-dependent and transport properties. Renormalization group theory is used to create new local potential models between nodes, within the approximation of local thermodynamical equilibrium. Assuming that these potentials give an average description of node dynamics, we calculate thermal and mechanical properties. If this method can be sufficiently generalized it may form the basis of a multiscale molecular dynamics method with time and spatial coarse graining.

Predicting macroscopic properties of materials starting from an atomistic or electronic level description can be a formidable task due to the many orders of magnitude in length and time scale that need to be spanned. A characteristic of successful approaches to this problem is the systematic coarse graining of less relevant degrees of freedom in order to obtain Hamiltonians that span larger length and time scales. For example, in first-principles thermodynamics of crystalline solids, which is one of the best developed examples of micro- to macrobridging, electronic and vibrational excitations are integrated out in order to obtain lattice-model Hamiltonians that describe the substitutional degree of freedom [1]. Monte Carlo simulations can then be used to simulate the kinetic evolution of the system or to obtain its thermodynamic state function. The reason first-principles thermodynamics has been so well developed is that it deals with extensive (averaged) quantities of homogeneous materials, and minor inhomogeneities in real materials, such as interfaces or dislocations, have a minor effect on the thermodynamic functions. Another extreme is the study of mechanical properties, such as plasticity, where the property of interest (i.e., plastic yield) is determined by discrete events (slip of dislocations), but over a very large scale. This type of problems requires the use of inhomogeneous coarse graining methods: atomistic-level resolution may be required near the key features in the material (e.g., dislocations or grain boundary) and lower resolution is needed in between, in order to make the problem computationally tractable. An important step towards such a coupled multi-length scale description was taken with the development of the quasicontinuum method (QCM) in which the behavior of groups of atoms (nodes) are treated with a finite element scheme [2]. The interaction between atoms is typically calculated with empirical potentials. In its original form QCM is essentially a method that improves the boundary conditions on atomistic regions and allows the boundary conditions of different atomistic regions to interact. Since QCM consists of an optimization of the energy, no time or temperature phenomena are present. Introducing temperature into QCM can be done by using potentials that incorporate the entropy due to lattice vibrations, for example, in a local Einstein description [3,4]. This is conceptually similar to the coarse graining of vibrations in first-principles thermodynamics [5] and leads to structures that are free-energy minimized. The study of time-/temperature-dependent phenomena is more difficult and requires the development of a dynamics for a system with an inhomogeneous level of coarse graining. To our knowledge, no formal development of this problem exists for a more general class of interactions, though methods that couple molecular dynamics to continuum description have been studied [6] and finite element dynamics has been developed in the harmonic approximation without time rescaling [7]. Other coarse graining techniques have been developed: effective Langevin dynamics procedures have been proposed to describe the relaxation of macroscopic degrees of freedom [8], and transition state theories have been generalized to boost time evolution, by modifying the shape of the surface of constant energy (hyperdynamics) [9] or using the Onsager-Machlup action [10]. None of these methods has employed simultaneous space/time coarse graining.

In this Letter we present a suggestion for the dynamical modeling of 2D systems that exist simultaneously at a different level of coarse graining in the time and space domains. Coarse graining requires both a scheme to remove atoms and a prescription to define potentials between the remaining atoms. For the approach advocated in this Letter, atoms are integrated out through bond moving, similar to the Migdal-Kadanoff approach in renormalization group (RG) [11]. New potentials can be defined in various ways, but important aspects are that the coarse grained system ultimately evolves to the same equilibrium state of the fully atomistic one, and the information

removed from the original system can be quantified, by the entropy contribution of each coarse graining. Hence, our criterion for defining new potentials when removing atoms is that the partial partition function of the system remains unchanged. We assess the validity of the model by comparing the elastic, thermodynamic, and transport properties of an inhomogeneously coarse grained and fully atomistic model.

As a matter of introduction, the coarse graining is first considered for a one-dimensional system. Let us consider a finite one-dimensional chain of atoms with mass m that interact through nearest neighbor pair potentials. Each particle has kinetic and potential energy and the total Hamiltonian is $H[\{q_i, p_i\}]$, where q_i is the position coordinate and p_i is the momentum. It will be assumed that the gradient of temperature along the chain is small enough for local thermodynamic equilibrium to exist. One coarse graining step is defined as removing every second atom. The energy $H_{(1)}(q_i, q_{i+2})$ between nearest neighbors of the coarse system (second neighbors in the full atomic system) is defined so as to conserve the partition function [the subscripts (1) indicate the first step of renormalization]:

$$e^{-\beta H_{(1)}(q_i, q_{i+2})} = \frac{1}{h} \int \int dq_{i+1}\, dp_{i+1}$$
$$\times\, e^{-\beta[H(q_i, q_{i+1}) + H(q_{i+1}, q_{i+2})]}.$$

Integrating the momenta leads to the reduced formula (integration at fix volume):

$$e^{-\beta[V_{(1)}(q_i, q_{i+2}, T) + \tilde{F}_{(1)}(T, i+1)]} = \int dq_{i+1}$$
$$\times\, e^{-\beta[V(q_i, q_{i+1}) + V(q_{i+1}, q_{i+2})]},$$

where $\tilde{F}_{(1)}(T, i+1)$ is an excess free energy that does not depend on the positions (q_i, q_{i+2}), in first approximation. It contains the entropy of atom $i+1$ lost in the renormalization step (removed information). It is necessary to keep track of this quantity to calculate properly the extensive thermodynamic quantities of the system. Finally, from the last equation, it is possible to extract an effective potential $V_{(1)}(q_i, q_{i+2}, T)$ which is temperature dependent, generally.

It is not obvious that this choice for the coarse graining algorithm leads to the correct dynamics. However, it is well known that the interaction so defined between particles i and $i+2$ is correct in the long time limit, i.e., when the motion of $i+1$ is much faster than i and $i+2$. Hence low frequency dynamics in the coarse grained system will likely be better represented than high frequencies. However, we feel that the ultimate justification for this approach should be evaluated on the basis of a comparison of properties of the coarse and fully atomistic system. This is investigated in this Letter. Hence this potential generates some dynamics of particles i and $i+2$ by the averaged interaction of particle $i+1$. In a first approximation, we consider $\tilde{F}_{(1)}(T, i+1)$ to be independent from (q_i, q_{i+2})

and the potential $V_{(1)}$ to contain all the possible spatial dependencies of the remaining coordinates.

As is typical in dynamic renormalization group theories, integrating out degrees of freedom, leads to a time rescaling as $t_{(1)} = b^z t$, where $b = 2$ is our scaling factor and z is the dynamical exponent [12]. This exponent does not affect equilibrium properties and will be determined later. Coarse graining has to conserve the total mass, so we take $m_i^{(1)} = m_i + m_{i+1}/2$ and $m_{i+2}^{(1)} = m_{i+2} + m_{i+1}/2$. To describe the potential we take a simple expansion around the minimum a ($a = 3$ Å atomistic lattice spacing and $m_i = 30 \times$ neutron mass), $V(q_i, q_{i+1}) = \sum_n k_n (q_i - q_{i+1} - \alpha_n a)^n$. A symmetric potential has $\alpha_n = 1$, $\forall n$. If we assume that the potential $V_{(1)}$ has the same functional shape of V, we get recursive relations $V_{(j-1)} \overset{\text{RG}}{\Rightarrow} V_{(j)}$ (with $V_{(0)} \equiv V$) which creates higher order coarse grained potentials:

$$V_{(j)}(q_i, q_{i+b^j}, T) = \sum_n k_{(j)_n} n(T)$$
$$\times\, (q_i - q_{i+b^j} - b^j \alpha_{(j)_n} a)^n.$$

In the simplified case of a harmonic potential $V(q_i, q_{i+1}) \equiv k_2(q_{i+1} - q_i - a)^2/2$ it can easily be shown that this renormalization of potential and mass preserves the dispersion relation for phonons with small momentum. The potential renormalizes to $k_{(1)2} = k_2/2$ (temperature independent). For a 1D chain $\omega(k_{ph}) = \sqrt{k_2/m} \, |\sin(ak_{ph}/2)|$ so that $\omega_{(1)}(k_{ph}) = \sqrt{(k_2/2)/(2m)} \times |\sin(2ak_{ph}/2)|$, hence $\omega(k_{ph}) \approx \omega_{(1)}(k_{ph})$ for small k_{ph}.

Our model system interacts through a potential with second and fourth powers $k_2 = 8.8 \times 10^3$ [K/Å^2], $k_4 = 1.8 \times 10^5$ [K/Å^4], which is either symmetric ($\alpha_2 = \alpha_4 = 1$) or nonsymmetric ($\alpha_2 = 0.999, \alpha_4 = 1.0315$), and we keep only the second and fourth power coefficients $k_{(j)_2}, k_{(j)_4}, \alpha_{(j)_2}, \alpha_{(j)_4}$ for every renormalized potential. To extend the method to a 2D lattice, we use the Migdal-Kadanoff moving bond (Fig. 1) approximation [11], to remove atoms.

The model and assumptions are tested by comparing the results of molecular dynamics simulations on the original fully atomic system and the inhomogeneously coarse grained system. Regions with different coarse graining
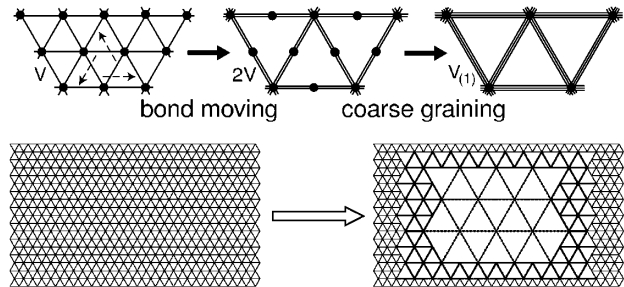

FIG. 1. Triangular lattice with bond moving approximation, and an example of inhomogeneous coarse graining.

are considered with different time evolution, because of the dynamical exponent z in the time scaling. The method is tested on *elastic properties, thermodynamic quantities, thermal expansion*, and finally on its *heat transport*. We see these as successfully more stringent tests to pass. A 2D triangular lattice with 225×31 atoms (6975 atoms) and symmetric potential is studied in response to static tensile/shear stress and under isotropic pressure deformation. The inhomogeneously coarse grained system is represented by 1510 nodes in an arrangement similar to that in Fig. 1. We calculate the strain response to a normalized tensile stress ($\sigma_{11}^{\star} = \sigma_{11}/\sigma_0$) along the longest direction (σ_0 is the tensile stress which gives 5% of lattice distortion). Various simulations are done at different normalized temperatures ($T^{\star} = T/T_0 = 0.04-0.64$, where $T_0 = \hbar\omega_0/k_B$, $\omega_0 = \sqrt{k_2/m}$). Figure 2 shows the strain response for $T^{\star} = 0.32$. The linear/nonlinear regions of the strains are clearly conserved by the inhomogeneous coarse graining. The elastic moduli of the two systems are equal to within 4%. Similar results have been obtained for shear strain (5%). For the bulk modulus calculations we use the nonsymmetric potential, as described in the previous section. In the range of temperatures considered the bulk moduli B_h for the original system (subscript h) and B_{ih} for the inhomogeneous coarse grained system (subscript ih) are equal to within $\pm1\%$. The good agreement for the elastic properties may not be surprising but indicates that the bond folding does not modify the macroscopic energies. Since the elastic properties are largely a reflection of the direct interaction and are not much influenced by temperatures or atomic motion, they do not really test the assumption made on the coarse grained dynamics.

We also evaluate the heat capacity for the 2D system with nonsymmetric potential. The heat capacity from the coarse system cannot be directly compared to the complete system, but needs to be augmented with the contribution from the entropy that is lost by removing degrees of freedom. This entropy can be calculated by keeping track of all the free energies $\tilde{F}_{(j)}(T, i)$ produced by the renormalization integration and taking temperature derivatives to get
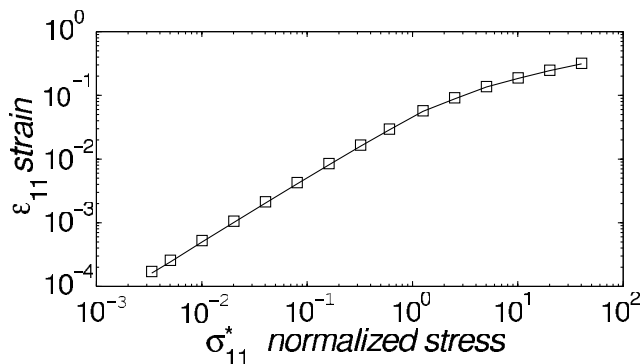
entropies [13]. We find that within the range of simulations $T^{\star} = 0.1-1.6$, C_{Vih} and C_{Vh} are equal to within the numerical noise of $\pm0.2\%$. Since the calculation is classical, the specific heats do not go to zero for $T^{\star} \to 0$.

The calculation of properties at constant pressure, such as thermal expansion or C_p, requires a particular effort to reproduce the correct dependence of free energy on temperature and volume. This dependence is hidden in either the nonlinear terms of the renormalized potentials or the volume dependence of the integrated free energy $\tilde{F}_{(j)}(T, i)$. An approximate representation of the thermal expansion can be achieved by interpolation of $\alpha_{(j)_2}$, $\alpha_{(j)_4}$ to conserve the thermalized bond length $\langle q_{i+b^j} - q_i\rangle_{(j)} = b\langle q_{i+(b-1)^j}^j - q_i\rangle_{(j-1)}$ (the subscripts on the averages indicate the potential used for the calculation). This constraint can be satisfied with a very small shift ($\approx 10^{-5}-10^{-4}$) of the parameters $\alpha_{(j)_2}$, $\alpha_{(j)_4}$. The overall effect is simply an effective bias on the potential to match the correct thermal expansion. Simulations with this method for the thermal expansion coincide with the homogeneous and the inhomogeneous coarse grained systems, within the numerical noise ($\pm5\%$). It is important to understand that, without this correction, coarse grained systems have incorrect thermal expansion (due to the removal of volume-dependent entropy). Hence simulations with *inhomogeneously* coarse grained regions would build up large internal strains upon changing the temperature, a fact that does not seem to have been recognized in previous formulations.

As stated in the description of the model, it is necessary to calculate a dynamical property (such as the thermal conductivity κ) to get the value of the dynamical exponent z. For finite systems, we can compare the results of a homogeneous lattice to those of an inhomogeneously renormalized lattice, if we assume the effects of finite size to be the same. To determine κ, several simulations of a 2D homogeneous triangular lattice ($N_x \times N_y = 225 \times 33$) and its homogeneously coarse grained equivalent are run at various temperatures. A nonsymmetric potential, which allows anharmonic phonon interactions, is used. Since there are no interfaces in the homogeneously coarse grained lattice, the only effect is due to the time scaling. The thermal
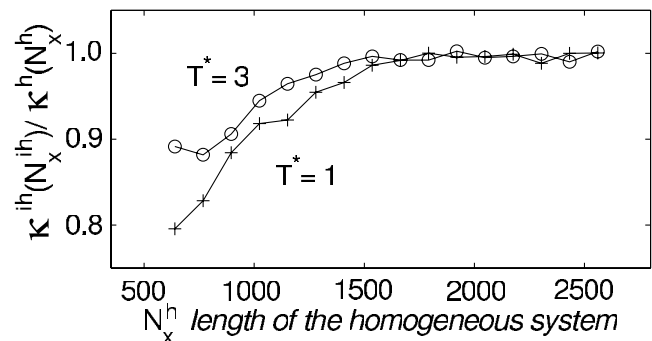

FIG. 2. Strain versus normalized stress $\sigma_{11}^{\star}$. The continuous line represents the strain ϵ_{h11} for the original system, while the squares ($\square$) represent the strain ϵ_{ih11} for the inhomogeneously coarse grained system ($T^{\star} = 0.32$).

FIG. 3. Interface effect: thermal conductivity ratio $\kappa^{ih}(N_x^{ih})/\kappa^h(N_x^h)$ versus the length of a 2D lattice with one interface. ($+$) for $T^{\star} = 1$ and ($\circ$) for $T^{\star} = 3$.
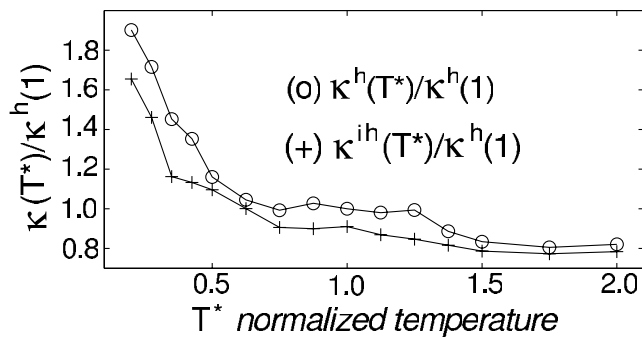
FIG. 4. Thermal conductivities $\kappa^h(T^\star)/\kappa^h(T^\star = 1)$ (○) and $\kappa^{ih}(T^\star)/\kappa^h(T^\star = 1)$ (+) of 2D lattices for various normalized temperatures.

conductivity κ is obtained from the standard Green-Kubo relation [14]. This relation involves time integration, so the dynamical exponent z can be implicitly obtained by fitting κ which is defined per "unit time." We find that for a value of $z \approx 1.45 \pm 0.1$, perfect agreement exists for the κ in the atomistic and coarse system.

In order to study the thermal transport in inhomogeneous systems the effect of interfaces between differently coarse grained regions needs to be understood. We run simulations for a 2D homogeneous lattice, with $N^h = N_x^h \times N_y^h$ atoms, and for its inhomogeneous coarse grained version, with $N^{ih} = N_x^{ih} \times N_y^{ih}$ nodes. The inhomogeneous lattice has one coarse graining interface at the center parallel to the y direction. To one side of this interface everything is fully atomistic, while to the other side one level of coarse graining is applied. Thus $N_x^{ih} = 2N_x^h/3$, and each region is $N_x^h/3$ wide. By systematically varying the size of the systems and plotting $\kappa^{ih}(N_x^{ih})/\kappa^h(N_x^h)$, we determine the effect of the interface/size in the thermal conductivity.

Figure 3 shows this effect at $T^\star = 1$ and 3: at high N_x^h, the length of the regions becomes comparable to the phonon mean-free path. Hence the fact that there are less nodes in the coarse grained system becomes less apparent and $\kappa^{ih}(N_x^{ih}) \rightarrow \kappa^h(N_x^h)$. The figure shows that, for our potential, dynamical exponent $z = 1.45$, and temperatures ($T^\star = 1$ and 3), regions wider than 500 nodes ($N_x^h/3$) give acceptable results.

For high enough separation between interfaces, the coarse grained dynamics reproduces the T dependence of the thermal conductivity well. Figure 4 shows $\kappa^{ih,h}(T^\star)/\kappa^h(T^\star = 1)$ for a 2D lattice with $N^h = N_x^h \times N_y^h = 11\,264 \times 33 = 371\,712$ atoms, and its inhomogeneous coarse grained version with $N^{ih} = 63\,072$ nodes, and six interfaces parallel to the y axis (each region is 512 nodes wide at different levels of coarse graining). The inhomogeneous model underestimates the thermal conductivity at low temperatures ($T^\star < 1/3$). At high temperatures ($T^\star > 1$) the two results are within 10% $\sim$ 15%. Normal materials have T_0 of the order of room temperature, so the error is acceptable considering the strong approximations in the method.

To conclude, we have proposed and analyzed a molecular dynamics method with time and spatial coarse graining. We show that mechanical and thermodynamical properties are in excellent agreement with the noncoarse grained system. If this method can be sufficiently generalized in 3D, it may form the basis of a RG multiscale molecular dynamics to investigate effects of temperature and defects in real nanostructures.

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