Dynamics and thermodynamics of a system with multiple length scales

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ABSTRACT

Descriptions, in which matter can be coarse grained to arbitrary levels, are necessary to study materials phenomena simultaneously at various length scales. Attempts to do this in the static regime have already been developed. In this work, we present an approach that leads to a dynamics for such coarse-grained models. Renormalization group theory is used to create new local potentials between nodes. Assuming that these potentials give an averaged description of node dynamics, we calculate thermal, mechanical and transport properties. If this method can be sufficiently generalized it may form the basis of a Molecular Dynamics method with time and spatial coarse-graining.

INTRODUCTION

Multiscale analysis of material properties starting from an atomistic 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 effective Hamiltonians that span larger length and time scales.

The different approaches developed up to now, can be divided in two main groups: mechanical and thermodynamical. In the mechanics approach, atoms are summed into groups and the interaction between these groups can be derived easily from the underlying atomic-level energies. Elastic theory can be seen as the homogeneous macroscopic limit of this. An example of this formalism is the quasicontinuum method (QCM) [1]. 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 [2], and leads to structures that are free-energy optimized. In the thermodynamics approach, atoms are grouped into different configurations, and statistical-energetic properties are calculated summing over all the available configurations with their proper statistical weight. To our knowledge, no formal development of the thermodynamical approach exists for a general class of interactions, though methods that couple Molecular dynamics to continuum description have been studied [3] and Finite Elements dynamics has been developed in the harmonic approximation without time rescaling [4]. Other coarse-graining techniques have been developed based on Langevin dynamics [5], on transition state theories (hyper-dynamics) [6], and on the Onsager-Machlup action [7]. Unfortunately, none of these methods has employed simultaneous space/time coarse-graining. It is clear that a theory able to bridge the two different coarse-graining approaches (mechanics and thermodynamics), would enormously extend our investigation capabilities in multiscale modeling.

In this work 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 work atoms are integrated out through bond moving, similar to the Migdal-Kadanoff approach in renormalization group [8] (figure 1). New potentials can be defined in various ways, but an important aspect is that the coarse-grained system ultimately evolves to the same equilibrium state of the fully atomistic one. 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 a non-homogeneously coarse-grained and fully atomistic model.

![Figure 1: Triangular lattice with bond moving approximation, and example of non-homogeneous coarse graining](image)

**THEORY**

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 $\mathcal{H}(q_i, q_{i+2})$ between nearest neighbors of the coarse system (2nd neighbors in the full atomic system) is defined so as to conserve the partition function (the subscripts $(1)$ indicate the 1st step of renormalization):

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

(1)

Integrating the momenta leads to the the reduced formula:

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

(2)

where $\tilde{\mathcal{F}}(T, i+1)$ is an excess free energy that does not depend on the positions $(q_i, q_{i+2})$. It contains the entropy of atom $i + 1$ lost in the renormalization step. 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 $\mathcal{V}(q_i, q_{i+2}, T)$ (with harmonic potentials the linear chain model can be solved analytically). This potential is now temperature dependent (the renormalized potential does not depend on the temperature if the original potential is harmonic, because of the gaussian integration).

It is not obvious that this choice for the coarse-graining algorithm leads to the correct dynamics. However is 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 that $i$ and $i+2$. Hence low frequency dynamics in the coarse 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 work. 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 $F_{(1)}(T, i+1)$ 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 [9]. This exponent does not affect equilibrium properties and will be determined later. Coarse graining has to conserve the total mass, so, we take, $m_{(1)} = m_i + m_{i+1}/2$ and $m_{(2)} = m_{i+2} + m_{i+1}/2$. To describe the potential we take a simple expansion around the minimum $a (a = 3 \text{ Å} \text{ atomic lattice spacing and } m_i = 30 \text{ neutron mass}), V(q_i, q_{i+1}) = \sum_n k_n (q_i - q_{i+1} - \alpha_n a)^n$. 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 $V_{(j-1)} \xrightarrow{RG} V_{(j)}$ (with $V_{(0)} \equiv V$) which creates higher order coarse-grained potentials:

$$V_{(j)}(q_i, q_{i+b}, T) = \sum_n k_{(j)n}(T)(q_i - q_{i+b} - b^j \alpha_{(j)n}a)^n.$$  \hspace{0.5cm} (3)

Our model system interacts through a potential with second and fourth powers $k_2 = 8.8 \cdot 10^3$ [K/Å$^2$], $k_4 = 1.8 \cdot 10^5$ [K/Å$^4$], which is either symmetric ($\alpha_2 = \alpha_4 = 1$), or non-symmetric ($\alpha_2 = 0.999, \alpha_4 = 1.0315$), 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 bonds (fig.1) approximation [8], to remove atoms.

**DISCUSSION**

The model and assumptions are tested by comparing the results of molecular dynamics simulations on the original fully atomic system and the non-homogeneously coarse grained one. Regions with different 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 $225 \times 31$ atoms (6975 atoms) and symmetric potential, is studied in response to static tensile/shear stress, and under isotropic pressure deformation. The non-homogeneously coarse grained system is represented by 1510 nodes in an arrangement similar to that in figure 1. We calculate the strain response to a normalized tensile stress $(\sigma_{11}^* = \sigma_{11}/\sigma_0)$ along the longest direction $(\sigma_0$ is the tensile stress which gives 5% of lattice distortion). Various simulations are done at different normalized temperatures $(T^* = T/T_0 = 0.04 \cdots 0.64$, where $T_0 = h\omega_0/k_B$, $\omega_0 = \sqrt{k_2/m})$. Figure 2 shows the strain response for $T^* = 0.32$. The linear / non-linear regions of the strains, are clearly conserved by the non-homogeneous coarse graining. The elastic modulus 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 non-symmetric potential, as described in
the previous section. In the range of temperatures considered the bulk modulus $B_h$ for the original system (subscript $h$) and $B_{nh}$ for the non-homogeneous coarse grained one (subscript $nh$) are equal to within $\pm 1\%$. The good agreement for the elastic properties may not be surprising but indicates that the bond-folding does not modify the macroscopic energies. As 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 non-symmetric potential. The heat capacity from the coarse system can not 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 [10]. We find that within the range of simulations $T^* = 0.1 \cdots 1.6$, $C_{Vnh}$ and $C_{Vh}$ are equal to within the numerical noise of $\pm 0.2\%$. Since the calculation is classical, the specific heats do not go to zero for $T^* \to 0$.

The calculation of properties at constant pressure, such as thermal expansion or $C_p$, requires 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

$$< q_{i+b} - q_i >_{(j)} - b < q_{i+(b-1)}^j - q_i >_{(j-1)},$$

(4)

(the subscripts on the averages indicate the potential used for the calculation). This constrained can be satisfied with a very small shift ($\approx 10^{-5} \sim 10^{-4}$) 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 for the homogeneous and the non homogeneous coarse grained systems, within the numerical noise ($\pm 5\%$). 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.

Figure 3: (A, left) Interface effect: thermal conductivity ratio \( \kappa_{nh}(N_{x}^{nh})/\kappa_{h}(N_{x}^{h}) \) versus the length of a 2D lattice with one interface. (+) for \( T^* = 1 \) and (o) for \( T^* = 3 \). (B, right) Thermal conductivities \( \kappa_{h}(T^*)/\kappa_{h}(T^* = 1) \) (o) and \( \kappa_{nh}(T^*)/\kappa_{h}(T^* = 1) \) (+) of 2D lattices for various normalized temperatures.

As stated in the description of the model, it is necessary to calculate a dynamical property (such as the thermal conductivity \( \kappa \)), to get the value of the dynamical exponent \( z \). For finite systems, we can compare the results for a homogeneous lattice to those of a non-homogeneously renormalized one, if we assume the effects of finite size to be the same. To determine \( \kappa \), several simulations for a 2D homogeneous triangular lattice \( (N_{x} \times N_{y} = 225 \times 33) \) and for its homogeneously coarse grained equivalent are run at various temperatures. A non-symmetric 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. Finally the dynamical exponent \( z \) can be implicitly obtained by fitting \( \kappa \) 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 \( \kappa \) in the atomistic and coarse system.

In order to study the thermal transport in non-homogeneous systems the effect of interfaces between differently coarse-grained regions needs to be understood. We run simulations for a 2D homogeneous lattice, with \( N_{x}^{h} = N_{x}^{nh} \times N_{y}^{h} \) atoms, and for its non homogeneous coarse grained version, with \( N_{x}^{nh} = N_{x}^{nh} \times N_{y}^{nh} \) nodes. The non homogeneous lattice has one coarse-graining interface at the center parallel to \( y \) direction. To one side of this interface everything is fully atomistic, while to the other side one level of coarse-graining is applied. Thus \( N_{x}^{nh} = 2N_{x}^{h}/3 \), and each region is \( N_{x}^{h}/3 \) wide. By systematically varying the size of the systems and plotting \( \kappa_{nh}(N_{x}^{nh})/\kappa_{h}(N_{x}^{h}) \), we determine the effect of the interface/size in the thermal conductivity. Figure 3A shows this effect at \( T^* = 1 \) 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 \( \kappa_{nh}(N_{x}^{nh}) \rightarrow \kappa_{h}(N_{x}^{h}) \). The picture shows that, for our potential, dynamical exponent \( z \approx 1.45 \), and temperatures \((T^* = 1 \text{ and } 3)\), 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 3B shows \( \kappa_{nh,h}(T^*)/\kappa_{h}(T^* = 1) \) for a 2D lattice with \( N_{x}^{h} = N_{x}^{h} \times N_{y}^{h} = 11264 \times 33 = 371712 \) atoms, and its non-homogeneous coarse grained version with \( N_{x}^{nh} = 63072 \) nodes, and 6 interfaces parallel to \( y \) axis (each region is 512 nodes wide at different level of coarse graining). The non-homogeneous model
underestimates the thermal conductivity at low temperatures ($T^* < 1/3$). At high temperatures ($T^* > 1$) 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 non-coarse grained system. If this method can be sufficiently generalized in 3D, it may form the basis of a RG Molecular Dynamics to investigate effects of temperature and defects in real nanostructures.

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References


