Exchange Monte Carlo for Molecular Simulations with Mono-electronic Hamiltonians

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We introduce a general Monte Carlo scheme for achieving atomistic simulations with mono-electronic Hamiltonians including the thermalization of both nuclear and electronic degrees of freedom. The kinetic Monte Carlo algorithm is used to obtain the exact occupation numbers of the electronic levels at canonical equilibrium, and comparison is made with Fermi-Dirac statistics in infinite and finite systems. The effects of a nonzero electronic temperature on the thermodynamic properties of liquid silver and sodium clusters are presented.

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In the recent years, the physics of materials and complex systems has undergone awesome development in the field of molecular simulation. Significant achievements include \textit{ab initio}, Car-Parrinello molecular dynamics (MD), linear-scaling, or progresses in ergodic techniques such as exchange Monte Carlo (EMC) and the Wang-Landau algorithm. Account of electronic structure is often made either implicitly with empirical potentials or more explicitly through one-electron methods, either in the framework of density-functional theory (DFT) or using tight-binding (TB) approximations. In the latter cases, the electronic ground state is described via integer occupation numbers. This is usually adequate for nonmetal systems. However the electronic states of metals can cross the Fermi surface, therefore integer occupations are not appropriate for continuous dynamics. Fractional occupation numbers must also be introduced for insulators or semiconductors, provided that the temperature is high enough for the lowest excited states to be populated.

Building upon a seminal paper by Mermin who extended the Hohenberg-Kohn theorem of DFT to nonzero electronic temperatures, several authors proposed to combine DFT and fractional occupation numbers. Most of these works were devoted to metals, and they tried to find suitable forms of the occupation laws for numerical stability purposes and a better sampling in the Brillouin zone. In particular, it was proposed to replace the Fermi-Dirac (FD) function with other expressions. Even when keeping a FD distribution, the best choice for electronic temperature was shown not to be necessarily related with the nuclear vibrational temperature. Additionally, and strictly speaking, the FD function holds for an infinite system, but should only be considered as an approximation when treating a small molecular system such as a metal cluster.

The goal of this Letter is to show how the true canonical equilibrium of both ionic and electronic degrees of freedom can be simulated through MC methods, for small or large sizes. A specific interest in choosing MC methods over MD simulations is their greater flexibility and wider range of application. They are very convenient for discrete systems, and they can be adapted using statistical biases to accelerate convergence. They also offer a straightforward way to sample grand-canonical ensembles, which is more difficult with MD. As seen below, the Monte Carlo method is well suited to the problem of electronic thermalization, especially for finite systems.

We consider the general class of materials modeled by mono-electronic Hamiltonians. At any given nuclear configuration \( \mathbf{R} \), the total energy \( E \) depends on the occupation numbers \( \{ n_i \} \). In the Kohn-Sham formalism, these numbers appear explicitly in the expression of the density, hence in the energy. In TB models, the band contribution is the weighted sum of the one-electron energies \( \{ \varepsilon_i \} : E(\mathbf{R}) = \sum_i n_i \varepsilon_i(\mathbf{R}) \). The first, most simple MC algorithm consists in treating the nuclear \( \{ \mathbf{R} \} \) and electronic \( \{ N \} \) degrees of freedom on the same footing, by performing random moves on the generalized coordinates \( \mathbf{Q} = (\mathbf{R}, \mathbf{N}) \). Here \( \mathbf{N} = \{ n_i \} \) is the set of instantaneous integer occupation states, which evolve during the simulation accordingly with the level statistics. In the Metropolis scheme, a change from \( \mathbf{Q}_{\text{old}} \) to \( \mathbf{Q}_{\text{new}} \) due to a change in either \( \mathbf{R} \) or \( \mathbf{N} \) is accepted with probability \( \text{acc}(\mathbf{Q}_{\text{old}} \to \mathbf{Q}_{\text{new}}) = \min[1, \exp(-\beta \Delta E)] \) where \( \Delta E = E(\mathbf{Q}_{\text{new}}) - E(\mathbf{Q}_{\text{old}}) \). The MC moves involving \( \mathbf{N} \) must keep constant the total number \( N \) of occupied states. The only moves of this kind that we consider are single exchanges between occupied and unoccupied, neighboring levels. For a given ionic geometry \( \mathbf{R} \), this algorithm clearly converges to the electronic canonical distribution in the ergodic limit.

The local moves involving \( \mathbf{R} \) and \( \mathbf{N} \) are now implemented in the framework of generalized ensembles. In our case, we use exchange Monte Carlo by performing simultaneous simulations at various temperatures. With some probability \( p \), exchange moves between \( \mathbf{Q}_t = (\mathbf{R}_t, \mathbf{N}_t) \) and \( \mathbf{Q}_j = (\mathbf{R}_j, \mathbf{N}_j) \) at the inverse temperatures \( \beta_t \) and \( \beta_j \), respectively, are attempted. They are accepted with the probability

\[
\text{acc}(\mathbf{Q}_t \leftrightarrow \mathbf{Q}_j) = \min[1, \exp(\Delta \beta \Delta E)].
\]

In this equation, \( \Delta \beta = \beta_t - \beta_j \) and \( \Delta E = E(\mathbf{Q}_t) - E(\mathbf{Q}_j) \). With probability \( 1 - p \), the usual local moves are attempted for all trajectories.

We test this algorithm on a model liquid silver, described by a TB Hamiltonian. In Fig. we have...
plotted the average radial density \( g(r) \) at \( T = 5000 \) K, from three different methods, for a system with 108 Ag atoms at constant density \( \rho = 10.5 \times 10^3 \) kg.m\(^{-3}\). The first method only considers nuclear moves, the electrons being frozen at \( T_e = 0 \). The second one is the previous MC method with adjacent trajectories at 2500 K and 7500 K, and \( p = 0.1 \). Finally, we perform a single trajectory MC calculation using only nuclear moves, but fractional occupation numbers given by the Fermi-Dirac distribution at \( T_e = T = 5000 \) K. For each atomic configuration, the chemical potential which normalizes \( \mathcal{N} \) is found by a Newton-Raphson minimization of the error function \( \chi^2(\mu) = \left[ \sum_k n_k^{FD}(\mu) - \mathcal{N} \right]^2 \) with \( n_k^{FD}(\mu) = \left[ 1 + \exp(\beta(\varepsilon_k - \mu)) \right]^{-1} \), starting from the distribution \( \mathcal{N} \) of the previous MC step. In this case, an entropic correction \( -T S \) to the energy is included with the usual form given by Mermin [6]:

\[
S = -k_B \sum_k n_k \ln n_k + (1 - n_k) \ln(1 - n_k).
\]

All simulations consist of \( 10^7 \) nuclear MC cycles. In the second method, \( \mathcal{N} \) electronic moves are attempted for each vibrational move.

The good agreement between the two calculations with \( T_e \neq 0 \) shows that the present MC algorithm is able to equilibrate both the electronic and nuclear degrees of freedom, for a quite large system whose electronic statistical distribution can be safely represented by a Fermi-Dirac distribution at the same temperature.

We now turn to finite atomic metal clusters. Finding the electronic average occupation numbers for any given nuclear geometry is a combinatorial task, which cannot be solved exactly in the canonical ensemble, except for very few (\( \lesssim 20 \)) levels. In the bulk limit, the grand-canonical ensemble is relevant and gives the FD distribution. For finite, intermediate sizes, the previous MC algorithm can solve this problem numerically. However, as is well known for discrete spin systems, exchange “flip” moves between occupied and unoccupied neighboring states can be expected to be mostly rejected at low temperatures \( T < \Delta E/k_B \), where \( \Delta E = E_{LUMO} - E_{HOMO} \) is the energy gap between the lowest unoccupied and highest occupied orbitals. The convergence can be greatly accelerated using the kinetic Monte Carlo (KMC) method [12] of Bortz, Kalos and Lebowitz. We use the KMC method in conjunction with the local exchange moves, starting from the \( T_e = 0 \) electronic distribution where only the lowest levels are populated. Tests on small clusters (up to 16 atoms) have shown that about \( 10^5 \) KMC steps are necessary to ensure convergence towards the exact statistical population. In Fig. 1, we plot the average occupation number at \( T = 500 \) K versus level energy for the ground state geometry of \( \text{Na}_{40} \) described by a TB Hamiltonian [13]. While the general shape is that of a Fermi-Dirac type, the actual FD distribution at electronic temperature \( T_e = 500 \) K does not match the result of the KMC calculation, which is best fitted by a FD law at effective temperature \( T_e^{ef} = 335 \) K.

We can combine the KMC algorithm for the electrons with the usual MC moves for the nuclei. To save computational time, the electronic problem is solved periodically, once every \( M \) steps. Again, the EMC strategy is used to improve global convergence and reduce quasi-ergodicity. However, one must be careful when attempting exchange moves between trajectories at different temperatures, because the energy depends explicitly on the nuclear coordinates, but also on temperature via the average occupation numbers. The same problem would hold for any other temperature-dependent potential, such as the effective potentials with quantum corrections used in liquids theory [14].

More precisely, the acceptance probability of an exchange between configurations \( \mathbf{R}_i \) and \( \mathbf{R}_j \) initially at the

![FIG. 1: Normalized radial density of liquid Ag at density \( \rho = 10.5 \times 10^3 \) kg.m\(^{-3}\) and vibrational temperature \( T = 5000 \) K.](image1)

![FIG. 2: Average occupation numbers for the electronic levels of \( \text{Na}_{40} \) at \( T = 500 \) K. The KMC results are compared with the FD statistics, for which the best fit is found at 335 K.](image2)
where \( \Delta E \) derivatives with respect to the occupation numbers are obtained numerically, their appearance due to this dependence. Unfortunately, because histograms methods [15] cannot be applied here. In ad

dependent energies, useful analysis techniques such as the clear and electronic coordinates can be simulated using as free energies. The canonical equilibrium of both entropic correction of Eq. (2) and should be considered covered. However, in the present case, they include the energies are temperature-independent, Eq. (1) is recovered. However, in the present case, they include the entropic correction of Eq. (3) and should be considered as free energies. The canonical equilibrium of both nuclear and electronic coordinates can be simulated using this MC method. Since we are dealing with temperature-dependent energies, useful analysis techniques such as the histograms methods [15] cannot be applied here. In addition, corrective terms to the thermodynamic properties appear due to this dependence. Unfortunately, because the occupation numbers are obtained numerically, their derivatives with respect to \( \beta \) are hard to get. We can reasonably assume that the corresponding effects are small at low temperature, since in bulk metals the electronic heat capacity is only a small quantity with a weak (linear) dependence upon temperature [13].

The previously described MC method is used to simulate the solidlike-liquidlike phase change in small sodium clusters. Recent theoretical works [17] emphasized the significant role of geometric (nuclear) effects on the caloric curves. However, the possible effects of electrons thermalization have not been considered yet. The influence of electronic temperature on shape was discussed by Yannouleas and Landman [18], but the jellium model used by these authors does not provide information about phase changes within an atomistic description. From the experimental point of view, the results by Haberland and coworkers [19] are still far from a complete understanding, especially the complex size-dependence of the thermal properties.

We first compare in Fig. 3 the heat capacity curves of \( \text{Na}_8 \) obtained without consideration of electron temperature, nor use of sophisticated sampling method [20], with the ones obtained with the present Monte Carlo algorithms. Here we can compute the exact average occupation numbers by solving the combinatorial problem for each configuration, or we can employ the numerical KMC procedure, both within the EMC scheme. 35 simultaneous trajectories were propagated with \( 10^7 \) cycles each, the occupation numbers being calculated for each configuration. For comparison, the curves obtained at \( T_e = 0 \) but with EMC moves are also plotted on Fig. 3. The resulting heat capacities show a very good agreement between the two present simulations with nonzero electronic temperature. Thus the KMC scheme provides a good approach to electronic thermalization. The thermodynamic curves obtained without using exchange MC, or assuming frozen electrons, are very similar. Therefore, in this case, we can conclude that (i) the electronic temperature plays only a small role; and (ii) EMC does not bring such an improvement over conventional Monte Carlo.

This situation becomes somewhat different for larger sizes. \( \text{Na}_{20}, \text{Na}_{40}, \text{Na}_{59}^+ \) and \( \text{Na}_{93}^+ \) are studied using the same methods except the one involving the exact calculation of the fractional numbers. Again, we also compare the heat capacities with our previous calculations. The whole results are shown in Fig. 4. The overall behavior resembles much that of Ref. [20], with a major peak in the heat capacity which marks the onset of the

![FIG. 3: Heat capacity per atom of \( \text{Na}_8 \), obtained from exchange Monte Carlo simulations with frozen (solid line) or thermalized (symbols) electrons. The average occupation numbers (full circles) are compared with the exact values (empty squares). The results of simple Monte Carlo of Ref. [21] are also shown for comparison (dashed lines).](image-url)

![FIG. 4: Heat capacities of sodium clusters calculated from exchange Monte Carlo simulations with frozen (solid lines) or thermalized (circles) electrons. Also shown for comparison are the results of simple Monte Carlo of Ref. [21] (dashed lines).](image-url)
solidlike-liquidlike phase change. However, two significant differences can be noted. First, the melting peak appears rather clearly, without any strong premelting feature (shoulder or peak) at low temperature. This must be contrasted with most other theoretical studies [4] which emphasized multistep melting in sodium clusters described by various models, but is consistent with experiments [4]. Second, the melting temperature indicated by the top of the peak is shifted to lower temperatures by about 10–30 K depending on size. Again this brings the present results closer to experiments, as our previous ones about 10–30 K depending on size. Again this brings the present results closer to experiments, as our previous ones

Extensions of the present algorithms to mean-field molecular Hamiltonians other than tight-binding is possible. A physical limitation is the relevance of the calculated excited levels as single-particle states and the neglect of many-body electron interactions. Another more important limitation is the difficult combination with molecular dynamics, due to the non-explicit dependence of the average occupation numbers on the nuclear structure, at least for finite systems. The use of Car-Parrinello dynamics including entropic corrections [24] requires some practical approximations, such as the Fermi-Dirac form for the occupation numbers, or the assumption that these numbers do not vary much during a short time scale.

The KMC scheme makes the present method naturally suited for use with Monte Carlo sampling of the nuclear degrees of freedom. Accelerating procedures [20, 25] for the total energy calculations in tight-binding models can also be a valuable improvement for large systems. The methods introduced in this Letter have a wide range of applications, for both finite and infinite systems, metals, insulators or semiconductor materials. They provide a numerically accurate way of calculating the fractional occupation numbers, and we gave evidences that the Fermi-Dirac statistical distribution is not appropriate for small clusters. Combined with advanced Monte Carlo techniques such as parallel tempering or the multicanonical ensemble sampling, these methods enable one to investigate the equilibrium thermodynamics of large complex systems which exhibit various kinds of phase transitions due to structural isomerization or electronic excitations. In this respect, clusters close to the insulator-metal crossover or having magnetic properties offer good candidates for further investigations.