"Fuzzy" Tight-Binding Monte Carlo Method: A $O(N)$ Technique for Calculating Structural and Electronic Properties of Materials

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We present a novel approach to computer simulations of the structural and electronic properties of materials that scales linearly with the number of electrons in the system. The approach is based on the following: (i) The introduction of a "fuzzy" Monte Carlo technique based on the approximate calculation of the total energy of the system. We show that a statistical error in the energy may be included in the thermal distribution via a new formulation of the Glauber dynamics of the Monte Carlo method. (ii) The calculation of the total energy via a recursion technique for a set of random initial states and a decomposition into individual atomic contributions. Applications to the simulation of liquid iron, silicon, and carbon are presented.

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The development of *ab initio* molecular dynamics techniques based on pseudopotentials and plane-wave basis sets can certainly be considered as a major step forward in the theory of the structural, electronic, and dynamics properties of complex systems [1–3]. The only drawback is that even on the fastest computers the application of these techniques is limited in practice to systems with $N \leq 100$ atoms, because for larger systems the computer time scales as N^3 as a consequence of the Pauli exclusion principle for the electrons imposing global orthonormalization constraints. Molecular-dynamics (MD) calculations within a non-self-consistent tight-binding (TB) framework allow one to treat systems with a few hundred atoms (typically $N \leq 300$), with still reasonably accurate results in many cases [4,5]. However, the $O(N^3)$ scaling problem remains unsolved. This problem of cubic scaling has clearly been recognized as the major obstacle to further progress in computational materials science, and a number of solutions have been proposed [6–10].

It is the purpose of this paper to propose a new access to "$O(N)$ techniques." Our approach is based on two essential ingredients: (1) We propose a new "fuzzy" Monte Carlo (MC) simulation technique which does not require the exact calculation of the total energy, but admits that the change ΔU in the total energy upon moving the atoms is known only within a certain statistical error. This error can be included in an effective thermal distribution. (2) The energy is calculated within a tight-binding framework at different levels of accuracy: (a) If one proceeds via exact diagonalization of the TB Hamiltonian, the error in ΔU results from the simultaneous move of *all* atoms. This leads to a very efficient TB-MC technique but still with $O(N^3)$ scaling. (b) If ΔU is deduced from the local electronic densities of state (DOS) calculated via the real-space recursion technique [11], $O(N^2)$ scaling is obtained. (c) If ΔU is calculated on the basis of a local decomposition of the total DOS calculated via the recursion technique for a set of random initial states, $O(N)$ scaling is achieved.

The fuzzy Monte Carlo method we propose is based on a reformulation of the standard Glauber dynamics [12]. Let ΔU be the change in the total energy of the system if its configuration changes from $\mathbf{r}$ to $\mathbf{r}'$ [in the following, we use $\mathbf{r}$ as a shorthand notation for the full set $(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ of atomic coordinates] and let ξ be a random number with the distribution

$$P_\xi(x) = \left[4k_BT\cosh^2\!\left(\frac{x}{2k_BT}\right)\right]^{-1}. \qquad (1)$$

Then the following algorithm is equivalent to the Glauber dynamics: (i) Generate the new configuration $\mathbf{r}'$ and compute ΔU. (ii) Generate the random number ξ with the distribution (1) (N.B.: If z is uniformly distributed in the interval $z \in (0,1)$, then $\xi = k_BT\ln[z/(1-z)]$ is distributed according to $P_\xi(x)$.) (iii) Set $Y = \Delta U + \xi$. (iv) If $Y \leq 0$, the transition from $\mathbf{r}$ to $\mathbf{r}'$ is accepted; for $Y > 0$ it is rejected.

The important thing to realize is that the distribution of ξ can be made to include a possible statistical error η in ΔU,

$$\Delta U = \overline{\Delta U} + \eta\,, \qquad (2)$$

where $\overline{\Delta U}$ is the exact value of the change in energy. In this case one sets

$$Y = \Delta U + \xi = \overline{\Delta U} + \eta + \zeta\,, \qquad (3)$$

with the relation $\xi = \eta + \zeta$ defining a new random variable ζ correcting the distribution. The probability distribution $P_\zeta(x)$ of the new variable is determined by the convolution

$$P_\xi(x) = \int_{-\infty}^{\infty} P_\eta(x')P_\zeta(x'-x)\,dx', \qquad (4)$$

where $P_\xi(x)$ is the correct thermal distribution [see Eq. (1)] and $P_\eta(x)$ is the statistical distribution of the errors η in ΔU (which is Gaussian according to the central limit theorem). In principle, Eq. (4) may be deconvoluted using fast-Fourier-transform techniques, but in practice it should be sufficient to approximate $P_\zeta(x)$ by

$$P_\zeta(x) \approx C P_{\xi^*}(x) + (1 - C)\delta(x), \qquad (5)$$

where $C \in (0,1)$ is a constant and P_{ξ^*} is the Glauber distribution (1) corresponding to a temperature T^*. C and T^* are determined by the condition that the second and fourth moments of the distributions of ξ and of $\eta + \zeta$ are equal (odd moments are zero). This leads to

$$C = \frac{7(1 - q^2)^2}{5q^4 - 10q^2 + 7} \qquad (6)$$

and

$$T^* = T\sqrt{(1 - q^2)/C} \qquad (7)$$

for the case of a Gaussian distribution of η with a second moment $\mu_2(\eta) = \sigma_\eta^2$ and $q^2 = \mu_2(\eta)/\mu_2(\xi) = \sigma_\eta^2/(\pi^2/3)(k_B T)^2$. The "fuzzy-MC" algorithm is then defined by the following: (i) For a proposed change of configuration from $\mathbf{r}$ to $\mathbf{r}'$, calculate $\Delta U(\mathbf{r}, \mathbf{r}')$, verify that it follows a Gaussian distribution, and determine the second moment $\mu_2(\eta)$. (ii) Calculate C and T^* according to Eqs. (6) and (7). (iii) Generate a uniformly distributed number $\nu \in (0,1)$. If $\nu \le C$, generate another uniformly distributed number $\lambda \in (0,1)$ and determine

$$Y = \Delta U(\mathbf{r}, \mathbf{r}') + k_B T^* \ln[\lambda/(1 - \lambda)]. \qquad (8)$$

If $\nu > C$, set

$$Y = \Delta U(\mathbf{r}, \mathbf{r}'). \qquad (9)$$

(iv) For $Y \le 0$ the transition $\mathbf{r} \rightarrow \mathbf{r}'$ is accepted, otherwise it is rejected.

This new MC algorithm has been tested against standard MC techniques. The standard procedure consists in sequential displacements of individual atoms. At each step, one has to calculate the contribution of one atom, say k, to $\overline{\Delta U}(\mathbf{r} \rightarrow \mathbf{r}') = U(\mathbf{R}_1, \ldots, \mathbf{R}'_k, \ldots, \mathbf{R}_N) - U(\mathbf{R}_1, \ldots, \mathbf{R}_k, \ldots, \mathbf{R}_N)$. The fuzzy MC allows one to calculate ΔU for a simultaneous move of all atoms,

$$\begin{aligned}\Delta U(\mathbf{r} \rightarrow \mathbf{r}') = {} & U(\mathbf{R}'_1, \ldots, \mathbf{R}'_k, \ldots, \mathbf{R}'_N) \\ & - (\mathbf{R}_1, \ldots, \mathbf{R}_k, \ldots, \mathbf{R}_N), \qquad (10)\end{aligned}$$

but to except or reject the atomic displacements from $\mathbf{R}_k$ to $\mathbf{R}'_k$ individually. To replace $\overline{\Delta U}$ by ΔU [Eq. (10)] results in an error

$$\eta_k = U(\mathbf{R}'_1, \ldots, \mathbf{R}'_k, \ldots, \mathbf{R}'_N) - U(\mathbf{R}_1, \ldots, \mathbf{R}'_k, \ldots, \mathbf{R}_N), \qquad (11)$$

but if the $\Delta\mathbf{R}_i = \mathbf{R}'_i - \mathbf{R}_i$ are random displacements with a Gaussian distribution, then η_k is again random with a Gaussian distribution. Its variance may be determined by a sampling, and the error may be included in the effective thermal distribution P_ξ [see Eqs. (2)–(9)]. Figure 1 compares the result of a classical MC calculation for liquid Fe at $T = 1840$ K (with the interatomic potentials described by effective two-body tight-binding-bond forces [13]) with a fuzzy-MC calculation performing a simultaneous move of all 1263 atoms in each step. The excellent agreement of both results testifies to the correctness of the fuzzy-MC method.

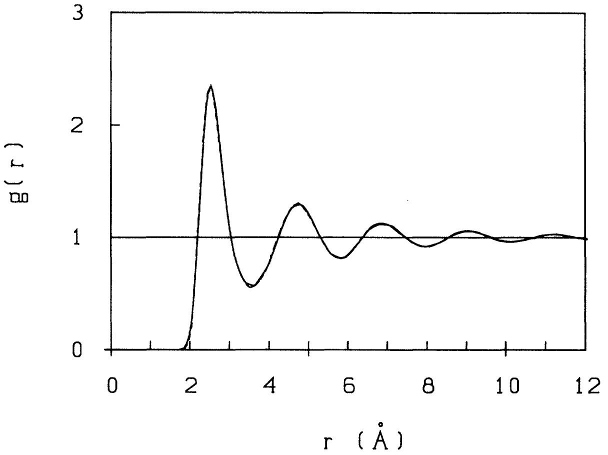

FIG. 1. Comparison of the pair distribution functions for liquid Fe, calculated via classical (broken lines) and fuzzy (full lines) MC.

The full power of the fuzzy-MC method is exploited in combination with a tight-binding calculation of the total energy of the system. It has been shown [14] that on the basis of local-density-functional theory and within a tight-binding framework, the total energy U may be written as a sum of a pairwise repulsive term U_{rep} describing the electrostatic, exchange-correlation, and nonorthogonality contributions and a bonding band-structure term $U_{\text{bs}}(\mathbf{r})$ given by the sum of the one-electron energy eigenvalues ϵ_n of the occupied states,

$$U = U_{\text{rep}} + \sum_{\epsilon_n \le E_F} \epsilon_n . \qquad (12)$$

At each MC move $\overline{\Delta U_{\text{bs}}}$ is calculated by diagonalizing the TB Hamiltonian $\mathbf{H}_{\text{TB}}$. Hence, with individual particle moves, the computational effort scales as N^4. The alternative is to displace the atoms simultaneously. But then the acceptance rate for stochastic moves decreases as $P_{\text{acc}} \propto (P_{\text{acc}}^1)^N$ (where P_{acc}^1 is the acceptance rate for single-particle moves). The fuzzy MC allows one to calculate ΔU for a simultaneous move of all atoms and leads to an $O(N^3)$ algorithm.

The next simplification consists in using the recursion method to calculate the contribution of each individual atom to ΔU_{bs} from the change in the local DOS upon a simultaneous move of all atoms. This leads to an algorithm with $O(N^2)$ scaling for relatively small ensembles (where the number of atoms within the interaction sphere of the TB Hamiltonian is of the same order of magnitude as the total number of atoms in the system). For very large systems the use of linked-cell algorithms for generating and storing the nearest-neighbor information [15] allows one to achieve even $O(N)$ scaling.

Finally, we can reduce the computational effort to a calculation of the total DOS, averaged over a set of initial states consisting of local orbitals with random phases, and use the technique proposed by Varga [16] to decompose the total DOS into a set of local DOS's that are then used to calculate ΔU_{bs}. Application of the recursion technique to an initial state $|u_0\rangle$ constructed by superposing the local orbitals $|i,\alpha\rangle$ with random phase factors $\exp(2\pi i \delta_{i,\alpha})$ [$\delta_{i,\alpha}$ uniformly distributed in (0,1)] leads to the total DOS $n(E) = \sum_n |w_n|^2 \delta(E - \epsilon_n)$ (with $w_n = \langle u_0 | \psi_n \rangle$ where ϵ_n and ψ_n are the eigenvalues and eigenstates, respectively, generated in the recursion sequence), plus a random error whose magnitude may be reduced by averaging over several random initial states. This error is added to the error arising from the simultaneous move of all atoms. The decomposition proposed by Varga is based on the observation that the weights $w_n^{i,\alpha} = \langle i,\alpha | \psi_n \rangle$ describing the contribution of the local orbital $|i,\alpha\rangle$ to the eigenstate $|\psi_n\rangle$, $n = 1,\ldots,L$ of an L-step recursion sequence may be expressed as

$$\begin{aligned} w_n^{i,\alpha} &= \sum_{m=0}^{L-1} \langle i,\alpha | u_m \rangle \langle u_m | \psi_n \rangle \\ &= \sum_{m=0}^{L-1} \langle i,\alpha | u_m \rangle P_m(\epsilon_n)\,, \end{aligned} \tag{13}$$

where $|u_m\rangle$ is the mth term in the recursively defined basis for the tridiagonal representation of $\mathbf{H}_{\mathrm{TB}}$ and the $P_m(\epsilon_n)$ are the orthogonal polynomials belonging to the eigenstate $|\psi_n\rangle$ and the eigenvalue ϵ_n (see Ref. [11]). The partial local DOS is then given by

$$n_{i,\alpha}(E) = \sum_{n=1}^{L} |w_n^{i,\alpha}|^2 |w_n|^2 \delta(E - \epsilon_n)\,. \tag{14}$$

Again, the stochastic fluctuations introduced by the random initial states may be controlled and included in the effective thermal distribution. In this form the fuzzy TB-MC algorithm has $O(N)$ scaling.

We have applied all three variants of the technique to calculate the structural and electronic properties of liquid carbon and silicon. The TB Hamiltonian is based on the optimized parametrization proposed by Goodwin, Skinner, and Pettifor [17]. Figure 2 shows the pair correlation functions of liquid silicon at $T = 1740$ K, calculated for a 512-atom ensemble using the $O(N^2)$ and $O(N)$ versions of the fuzzy TB-MC method [the $O(N^3)$ approach gives indistinguishable results]. The virtually identical results obtained by the different techniques demonstrate that the approximations used for the calculation of the single-particle energies are well controlled. Figure 3 compares the pair correlation functions for low-density amorphous carbon at $T = 5000$ K and $\rho = 2.0\ \mathrm{g\,cm^{-3}}$ with the TB-MD results of Wang, Ho, and Chan [18] and with the *ab initio* MD calculations of Galli *et al.* [19]. The good agreement with the earlier TB-MD [18] calculations based on the same Hamiltonian demonstrates that the fuzzy-MC technique is as accurate (the remaining small differences in the region of the first peak are within the statistical limits of the 64-atom ensemble used in TB MD) as conventional TB-MD methods. We also show the *ab initio* density-functional MD [19] results to demonstrate that the TB Hamiltonian leads to realistic results. We also note that the quadratic and linear techniques produce identical results.

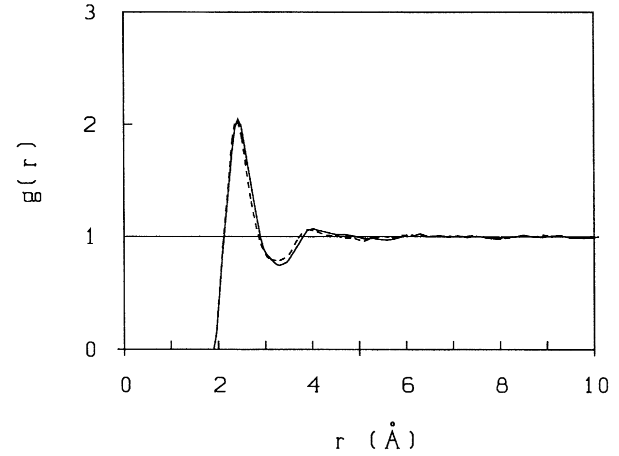

FIG. 2. Comparison of the pair correlation functions $g(R)$ for liquid Si, calculated for 512-atom ensembles using the $O(N)$ (full lines) and $O(N^2)$ (broken lines) fuzzy-MC algorithms. Compare text.

Figure 4 shows the scaling of the CPU per MC step with the number of atoms in the ensemble. The CPU times are for calculations on an IBM-RISC6000-375

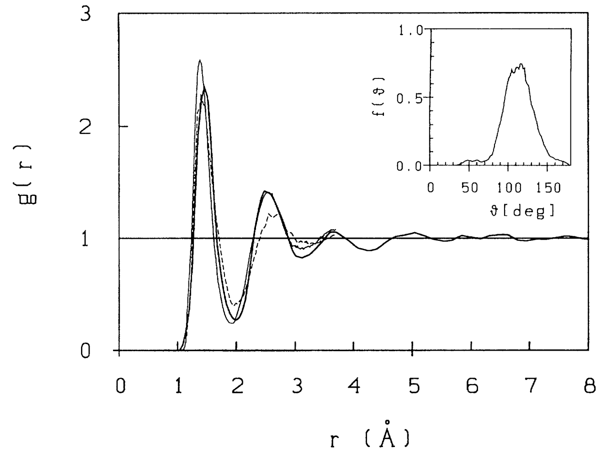

FIG. 3. Pair correlation function $g(R)$ and bond-angle distribution $f(\theta)$ (inset) for low-density liquid carbon at $T =$ 5000 K. Full line, present work (fuzzy TB MC with linear scaling for a 512-atom ensemble); thin lines, TB MD for a 64-atom ensemble and using the same TB Hamiltonian (after Wang, Ho, and Chan [18]); dashed lines, *ab initio* MD for a 64-atom ensemble (after Galli *et al.* [6]).

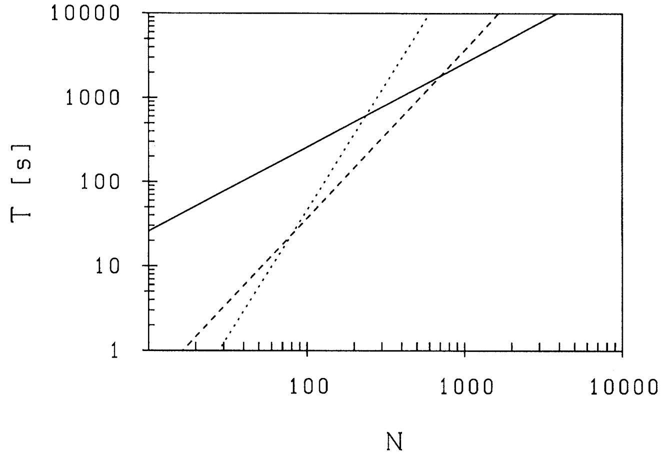

FIG. 4. Variation of the CPU time per MC step with the number of atoms in the $O(N^x)$ fuzzy TB-MC methods: full line, $x = 1$; dashed line, $x = 2$; dotted line, $x = 3$. The results given in the graph refer to *l*-Si described by the Goodwin-Skinner Hamiltonian. Compare text.

workstation. For the case of liquid Si we find that the $O(N^3)$ version is fastest up to $N = 80$, the $O(N^2)$ approach for $80 \leq N \leq 700$, and the $O(N)$ technique for $N \geq 700$. The CPU times per step are very similar to the values given by Ordejon *et al.* [7] for their more localized basis functions. Simulations for $N \simeq 1000$ are possible on fast workstations. However, the decisive parameter is the number of occupied eigenstates; hence, for systems with more electrons per atom (e.g., transition metals), these numbers will be lower by a corresponding factor. Temperature also has a certain influence as the error in $\Delta U_{\rm bs}$ must be reduced at lower T, e.g., by averaging the total DOS over a larger number of random initial states. We also note that the numbers given refer to a constant setting of all parameters, independent of the number of atoms. Using a "linked-cell" algorithm in conjunction with our "quadratic" method will allow one to achieve linear scaling for $N \geq 600-1000$. With our "linear" method, the number of random initial states may be reduced for large systems without loss of accuracy, so that even sublinear scaling may be achieved.

In conclusion, we have presented a new tool for performing mixed classical–quantum-mechanical simulations of the structural and electronic properties of materials. The basis of the technique is the combination of the advantages of the new fuzzy-MC algorithm with efficient real-space techniques for the calculation of the electronic spectrum. Simulations for $N \sim 1000$ atoms are possible even on fast workstations. We also remark that the technique has many features that make parallelization very easy.

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