Local Molecular Dynamics with Coulombic Interactions

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We propose a local, $\mathcal{O}(N)$ molecular dynamics algorithm for the simulation of charged systems. The long ranged Coulomb potential is generated by a propagating electric field that obeys modified Maxwell equations. On coupling the electrodynamic equations to an external thermostat we show that the algorithm produces an effective Coulomb potential between particles. On annealing the electrodynamic degrees of freedom the field configuration converges to a solution of the Poisson equation much like the electronic degrees of freedom approach the ground state in *ab initio* molecular dynamics.

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Coulomb's law for the interaction between two charged particles is generally presented as a static limit of Maxwell's equations valid after all transients have decayed to zero [1]. Because of the difference between the signal propagation speed c of electromagnetic radiation and excitations in condensed matter, almost all particle-based numerical simulations of materials employ the approximation of static, instantaneous interactions ($c = \infty$). This approach has some disadvantages. Since the electrostatic potential is the unique solution of Poisson's equation, even the slightest motion of particles requires a *global* recalculation of the electrostatic potential at every time step; this calculation can dominate the computational effort [2] and represents a major bottleneck for the development of efficient multiprocessor codes.

One might wonder whether more efficient code results from a formulation that allows one to reduce the propagation speed, but still maintains a sufficiently large separation of time scales in a manner familiar from *ab initio* molecular dynamics [3]. The ratio of the rms particle velocity $\bar{v}$ to c would play the role of an optimization parameter much like the ratio of electron to nuclear masses in quantum chemistry. In order to change c, one would simulate the evolution of the coupled particle-electromagnetic system as is routinely done in plasma physics [4]. Such a treatment has the great advantage of only requiring *local* operations, but requires an enormous reduction of c in order to be efficient. However, with such a dramatic reduction of c the electric field will not follow the particle motion adiabatically. In this limit there is no guarantee that the correct thermodynamic ensemble is generated. A fundamental question thus arises: Is Coulomb's law *just* a static limit of the Maxwell equations or is the law more general?

Recent work on Monte Carlo algorithms [5–7] has shown that the correct thermodynamic potential is found even if the particles and fields propagate at the same rate: If one writes that the energy of an electric field $\mathbf{E}$ is $\mathcal{U} = \int \mathbf{E}^2/2\, d^3\mathbf{r}$, then a Gibbs distribution characterized by interactions in $1/r$ is generated from the constrained integral

$$\mathcal{Z}(\{\mathbf{r}_i\}) = \int \mathcal{D}\mathbf{E} \prod_{\mathbf{r}} \delta(\mathrm{div}\mathbf{E}(\mathbf{r}) - \rho(\{\mathbf{r}_i\})) e^{-\mathcal{U}/k_B T}, \quad (1)$$

where the charge density, $\rho(\mathbf{r}) = \sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i)$; the charge of the ith particle is e_i. We work in Heaviside-Lorentz electromagnetic units where $\epsilon_0 \equiv \mu_0 \equiv 1$. The constraint in the δ functions is Gauss's law. In the electrostatic limit, $\mathbf{E} = -\mathrm{grad}\,\phi_p$, where ϕ_p is the solution of Poisson's equation with source ρ, but in general $\mathbf{E} = -\mathrm{grad}\phi_p + \mathbf{E}_{\mathrm{tr}}$, where $\mathbf{E}_{\mathrm{tr}}$ is an arbitrary transverse or rotational vector field. By changing variables and integrating over $\mathbf{E}_{\mathrm{tr}}$, one immediately sees [5,6] that the longitudinal field components result in a Coulombic partition function, while the contribution from the transverse components merely multiply this partition function by a constant. Thus Coulomb's law is valid even in the presence of a fully equilibrated and dynamic transverse electrostatic field. This result is nontrivial since the retarded interaction between two charges is not simply $1/r$ [1].

This Letter implements two molecular dynamics algorithms which sample Eq. (1). We show that our algorithms generate the correct thermodynamic potential and discuss the consequences of lowering c for time dependent correlations. The algorithms involve only *local operations* on the field degrees of freedom and the CPU time per integration step scales linearly with the number of particles N. The most obvious choice for sampling Eq. (1) is to directly integrate Maxwell's equations together with Newton's equations for the particles coupled to the electromagnetic field:

$$\begin{aligned} \dot{\mathbf{B}} &= -c\ \mathrm{curl}\,\mathbf{E}, & m_i \dot{\mathbf{v}}_i &= e_i \mathbf{E}(\mathbf{r}_i), \\ \dot{\mathbf{E}} &= c\ \mathrm{curl}\,\mathbf{B} - \mathbf{J}, & \dot{\mathbf{r}}_i &= \mathbf{v}_i, \end{aligned} \quad (2)$$

$\mathbf{J}$ denotes the electric current due to the particle motion. As in the electrostatic limit, we have dropped the Lorentz force $e_i(\mathbf{v} \times \mathbf{B})/c$ in the equation for $\dot{\mathbf{v}}_i$ [8].

Evolution of the system is described by a map in phase space. If the Jacobian of this map is unity then there is a conserved density, just like in Hamiltonian mechanics where Liouville's theorem can be applied: Let us integrate

Eqs. (2) through a time step δt and evaluate the Jacobian of the transformation $\partial x_i'/\partial x_j$ where x_i denotes any one of the variables in Eqs. (2). Since we have $\partial x_i'/\partial x_i = 1$, i.e., the diagonal elements of this matrix are unity we find that the Jacobian is $1 + O(\delta t)^2$. Thus in the limit of small time steps the Jacobian is preserved. This implies that a measure conserved by the dynamics is

$$d\mu = \prod_{i,\alpha} dr_{i,\alpha} dv_{i,\alpha} \prod_{\mathbf{r},\beta} dE_{\mathbf{r},\beta} dB_{\mathbf{r},\beta}, \tag{3}$$

where the products are over the particles and then all space. We note that generalized Liouville dynamics have turned out very useful recently in the construction of new thermostating methods for particle simulation [9]. Since the equations of motion conserve the energy $\mathcal{U}_m = \sum m\mathbf{v}_i^2/2 + \int d^3\mathbf{r}\{\mathbf{B}^2/2 + \mathbf{E}^2/2\}$ we deduce that the partition function for this system is $\mathcal{Z} = \int d\mu\, \delta(U_m - U_0) \times \delta$ (constraints) where the δ function includes all the constraints and conservation law inherent in the two Maxwell equations of Eqs. (2).

A standard hypothesis of ergodicity would lead us to guess that we now sample Eq. (1). However, the full Maxwell equations have associated with them many independent conservation laws in addition to the Gauss condition [10], most importantly $\mathrm{div}\mathbf{B} = 0$. If we simply integrate the Maxwell equations we have to supplement the Gauss constraint in Eq. (1) with many other constraints in such a way that the analytic formulation of the partition function becomes intractable. We should reduce the symmetries and conservation laws inherent in Maxwell's equations, leaving just Gauss's law; we do this by transforming to a constant temperature ensemble and coupling the electromagnetic field to thermostats to improve the ergodicity of the field degrees of freedom.

We modify two of the equations of motion to

$$\begin{aligned} \dot{m}\mathbf{v}_i &= q_i \mathbf{E}(\mathbf{r}_i) - \gamma_1 \mathbf{v}_i + \vec{\xi}_1, \\ \dot{\mathbf{B}} &= -c\,\mathrm{curl}\mathbf{E} - \gamma_2 \mathbf{B} + \vec{\xi}_2, \end{aligned} \tag{4}$$

where the damping γ_j and the noise $\vec{\xi}_j$ are related by the fluctuation dissipation theorem. The equation for the particle velocity is entirely conventional in molecular dynamics, that for the magnetic field less so. The noise $\vec{\xi}_2$ on the magnetic field degrees of freedom is completely general; it does not satisfy $\mathrm{div}\vec{\xi}_2 = 0$. Because of the coupling of $\mathbf{B}$ to the random noise it is ergodic, as is $\mathbf{v}_i$. Introduction of the noise has destroyed the unwanted constraints arising from Maxwell's equations. However, taking the divergence of $\dot{\mathbf{E}} = c\,\mathrm{curl}\mathbf{B} - \mathbf{J}$ we see that Gauss's law is still valid for the thermalized equations of motion if the equation of continuity $\mathrm{div}\mathbf{J} + \dot{\rho} = 0$ holds, and we start the simulation with an initial condition consistent with Gauss's law.

One can check that the distribution $P_0 = e^{-\beta U_m}$ is a fixed point of the thermalized equations. Such a demonstration is often taken as being a sufficient criterion for a thermostat in physics; due to presence of the conservation laws in Maxwell's equations we have examined convergence of the dynamics by studying the function [11] $H = \int [P(t) - P_0]^2/P_0 d\mu$ and calculating the dynamics of H with a Fokker-Planck equation for the full distribution function P. By requiring that $\dot{H} = 0$ we find that P must converge to a function of the form $P = \mathcal{A}(\mathbf{E}, \mathbf{r}_i)P_0$ where

$$\left[\int d^3\mathbf{r}(c\,\mathrm{curl}\mathbf{B} - \mathbf{J}) \cdot \frac{\partial}{\partial \mathbf{E}} + \sum_i \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i}\right]\mathcal{A} = 0. \tag{5}$$

The condition that this equation is valid for arbitrary $\mathbf{B}$ leads to the conclusion that $\mathcal{A}$ is a functional of only $\mathrm{div}\mathbf{E}$. The general solution of Eq. (5), is then a general functional of $\mathrm{div}\mathbf{E} - \rho$: $\mathcal{A} = \bar{A}[\mathrm{div}\mathbf{E}(\mathbf{r}) - \rho(\{\mathbf{r}_i\})]$. Choosing $\mathrm{div}\mathbf{E} - \rho = 0$ as a conserved initial condition then leads to the required result $P(t) \to P_0$. With the weight P_0 and the measure $d\mu$ we integrate over the Gaussian variables $\mathbf{B}$ and $\mathbf{v}_i$ and reproduce the required partition function Eq. (1) independent of c.

In our implementation of the algorithm, particles of mass m move in the continuum. We interpolated the charges onto the L^3/a^3 nodes of a cubic mesh using 3rd order B-splines, distributing the charge of each particle onto 27 nodes [7]; higher or lower order schemes are possible if they conserve charge. The same mesh is used to discretize the field equations, and the electric field $\mathbf{E}$ is associated with the $3L^3/a^3$ links. Groups of 4 links are grouped into plaquettes, and the magnetic field $\mathbf{B}$ lives on the $3L^3/a^3$ plaquettes [12]. The particles interact in addition with a shifted Lennard-Jones potential of scale a truncated at its minimum, $r_c = 2^{1/6}a$. This discretization is equivalent to a standard 7-point discretization of the Laplacian [13].

In order to integrate the equations of motion (2) of the coupled field/particle system, we use a standard velocity Verlet scheme. First we advance the magnetic field $\mathbf{B}$ together with the particle velocities to midpoint. Then, the values of the $\mathbf{B}$ field and the velocities are used to advance the electric field $\mathbf{E}$ and the positions $\mathbf{r}_i$. Finally, the Langevin thermostats Eqs. (4) are applied and the $\mathbf{B}$-field/velocity moves completed. We have used a standard time step $\delta t = 0.01\tau$, where $\tau = \sqrt{ma^2/\epsilon}$ is the unit of time and $\epsilon = e^2/a$ the unit of energy. The same time step is used for both the particle and field equations. The Courant criterion for the stable integration of Maxwell's equations is $\delta t < a/\sqrt{3}c$. For the values of c used in this Letter this criterion is always satisfied and never limits δt.

The success of the method relies on implementing constraint conserving couplings between particles and fields as well as exact local charge continuity. Motion of a particle leads to a local (finite) fluctuation of the interpolated charge density $\Delta\rho_l$. From this we construct a *local current* $\mathbf{J}_l$ such that $\mathrm{div}\mathbf{J}_l = -\Delta\rho_l$. We decompose the displacement of a particle $\Delta\mathbf{r}_i$ into a (time reversible)

sequence of steps $\{\Delta x/2, \Delta y/2, \Delta z, \Delta y/2, \Delta x/2\}$ [14]. Each substep in a direction α leads to a current in only those links parallel to α [15]. The field update is then slaved to the current $\Delta \mathbf{E} = -\Delta \mathbf{J}_l$. The force acting on the particles is found from the principle of virtual work: A fluctuation of a particle position $\delta\alpha$ induces a local charge fluctuation and thus a *local* current. The force is just $f_\alpha = -\delta U_m/\delta\alpha$ [16]. This prescription for the force leads to the usual electric force $f_{\rm el} = e_i\langle \mathbf{E}(\mathbf{r}_i)\rangle$, where $\langle \mathbf{E}(\mathbf{r}_i)\rangle$ is a local average of the electric field which depends on the exact form of the interpolation of the charge density to the lattice; this is the origin of the acceleration in Eq. (2).

The use of a lattice to discretize the Maxwell equations leads to artifacts in the interaction and self-energy of the particles. These artifacts are removed using dynamic subtraction [7]. A scalar field that couples to the interpolated charges via the energy functional $\mathcal{F}_Y[\psi] = \int[((\nabla\psi)^2 + \mu^2\psi^2)/2 - \rho\psi]d^3r$ leads to an effective interaction between particles of the form $V_Y(\mathbf{r}) = -e_i e_j e^{-\mu r}/r$, which when added to the direct Coulomb interaction regularizes the short distance singularity in $1/r$. In our molecular dynamics code this field obeys the equation of motion

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} = \nabla^2\psi - \mu^2\psi + \rho - \gamma_3\frac{\partial\psi}{\partial t} + \vec{\xi}_3. \qquad (6)$$

The Yukawa force $f_{\rm Y} = +e_i\langle {\rm grad}\psi\rangle$ on the particle comes from a local average consistent with the virtual work principle, and the total force reads $f = f_{\rm el} + f_{\rm Y} + f_{\rm LJ}$. We correct for the Yukawa potential by adding an extra analytic Yukawa potential (with opposite sign) to the truncated Lennard-Jones potential at short distances.

Our algorithm runs in two modes. In mode I, all auxiliary fields are kept at the same temperature as the particles, and we generate the correct thermodynamic interaction independent of $\bar{v}/c$. We also run in "dynamical simulated annealing mode" [3] (mode II), where we anneal the electric degrees of freedom to zero temperature by removing the noise on $\mathbf{B}$ and using larger values for γ_2 and c, while maintaining the finite temperature thermostat on the particles. In this case, our code is closer to traditional methods, because the field configuration converges to the solution of Poisson's equation when particle motion stops. This mode is clearly similar in approach to dynamic methods used in quantum simulations [3] with $\bar{v}/c$ a freely variable optimization parameter.

Our numerical tests of the algorithm begin with a direct verification of the $\mathcal{O}(\mathcal{N})$ scaling in Fig. 1 (open symbols). While the effort to integrate the auxiliary fields only depends on the number of grid points, the work required for the particle-field couplings rises linearly with N. At the "working density" of a typical biomolecular simulation using a 0.1 nm grid and particle volumes of $\mathcal{O}(0.01\ {\rm nm}^3)$ [13] (corresponding to $N \sim 3000$ in Fig. 1), both parts of the simulation contribute equally to the total time. Note, in particular, that the field integration is twice as fast as the reciprocal part of a standard Fourier-based implementation [17] (filled symbols). The expense for the particle-field couplings is higher in our code, but optimizations in the prefactor can be expected.

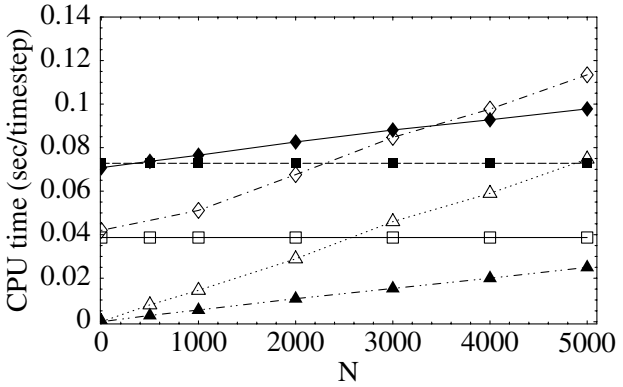

FIG. 1. Time for the field integration (□), field-particle couplings (△), and total time (◇) in a system of size $L = 30a$ as a function of N on an single AMD Athlon CPU. Also shown are results for the same system treated with a Fourier-based method using a charge interpolation of the same order (filled symbols, ■ corresponds to the total reciprocal work).

Next, we performed checks on the correctness of the method by placing two particles of opposite charges in a box and measured the instantaneous force. We compare the results to the short range expansion of the analytic

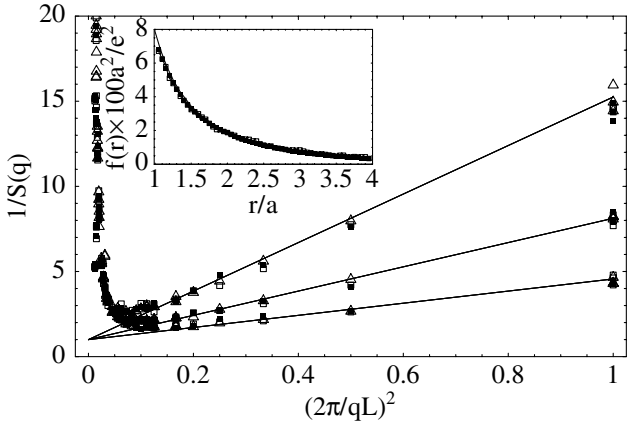

FIG. 2. Static structure factor $S(q) = \langle s(\mathbf{q})s(-\mathbf{q})\rangle$, $s(\mathbf{q}) = (1/\sqrt{N})\sum_i e_i \exp(i\mathbf{r}_i\mathbf{q})$ of a charged symmetric electrolyte ($L = 15a$); three densities $n = 0.05a^{-3}$, $n = 0.1a^{-3}$, $n = 0.2a^{-3}$, and $T = \epsilon/4\pi k_B$ using the present algorithm in mode I (□), $c = 1a/\tau$; transverse electric field and particles thermostated to $T = \epsilon/4\pi k_B$, $\bar{v}/c \approx 0.3$ using Eqs. (4) and (6). For ■, the electric field is damped, mode II, $c = 32a/\tau$, $\bar{v}/c \approx 0.01$. Also shown is a corresponding Monte Carlo simulation (△). Solid lines: Debye theory. Inset: average instantaneous force for a pair of charges, $L = 8a$ for modes I and II. Solid curve: $f = -dV/dr$, where $V = -1/4\pi r - r^2/6\epsilon_0 L^3$ from Ewald summation [20]. Lattice artifacts removed using dynamic subtraction, $\mu = 0.9/a$.

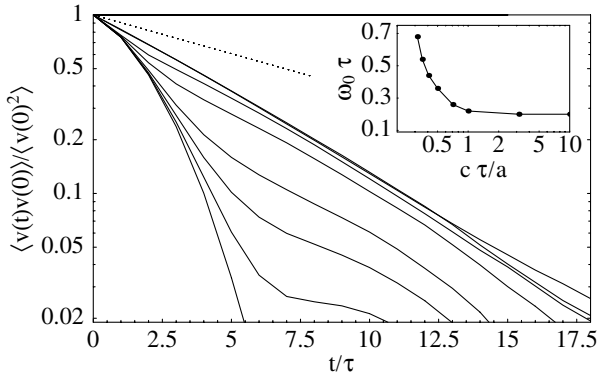

FIG. 3. Velocity autocorrelation functions for $L = 10a$, 50 particles, mode I. Intrinsic damping $\gamma_1 = 0.1\tau^{-1}$, dotted line: $\exp(-0.1t/\tau)$. Solid lines from left to right: correlations for $c = 0.32, 0.35, 0.41, 0.5, 0.7, 1, 3.2, 10a/\tau$. Inset: initial decay rate ω_0 from exponential fits.

Ewald summation in the inset of Fig. 2 and find excellent agreement for both modes. We also simulated a globally neutral electrolyte composed of positive and negative particles in order to observe the phenomenon of Debye screening. At high enough temperatures, we expect a static charge-charge structure factor of the form $S(q) = e^2q^2/(\kappa^2 + q^2)$ where the inverse Debye screening length $\kappa^2 = ne^2/k_BT$, n is the density of charge carriers. Figure 2 compares $S(q)$ for several densities with this expression and also to results measured with our related Monte Carlo algorithm [7]. Again we find good agreement. As described in [7] we also have studied the dispersion law of charge and density fluctuations in a homogeneous electrolyte and were able to confirm the fast equilibration of density-density and charge-charge correlations.

In Fig. 2, we showed that the algorithm generates a pair potential equivalent to that of the Ewald summation for two very different values of $\bar{v}/c$. However, particle dynamics are clearly sensitive to c. As a simple illustration, we show velocity autocorrelations $\langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle$ for several values of c in Fig. 3. For very dilute systems the autocorrelation is dominated by the damping constant γ_1 in the Langevin thermostat, and $\langle \mathbf{v}(t)\mathbf{v}(0)\rangle \sim \exp(-\gamma_1 t)$. At higher densities, this decay is modified by collisions, and $\langle \mathbf{v}(t)\mathbf{v}(0)\rangle$ has a faster decay. The curves in Fig. 3 are in this density regime and are sensitive to the intrinsic dynamics of the particles. For $c < 1a/\tau$, correlations are modified by the low propagation velocities, but saturate to a common curve for larger values of c.

We have simulated a charged system interacting via Coulomb forces using an algorithm in which the speed of light is a free variable. If $\bar{v}/c$ is large the dynamics generate the correct statistical mechanical ensemble for Coulomb interacting particles, but dynamic correlations are modified. On increasing c both the statistical mechanical and the local dynamical properties are reproduced correctly. The structure of our code is very similar to "particle in cell" plasma codes which are rather easy to implement on large multiprocessor computers with limited interprocessor bandwidth. We therefore expect that on many processors, our algorithm can be competitive with other fast electrostatic methods including Fourier [2], multigrid [18], and fast multipole methods [19]. Our method also generalizes naturally to situations with spatial dielectric inhomogeneities, which cannot be solved using Fourier techniques and nonstandard boundary conditions, e.g., irregularly shaped volumes.

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