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NONEQUILIBRIUM ATOMISTIC SIMULATIONS—METHODS AND RESULTS

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Steady diffusive, viscous, plastic, and heat-conducting flows have all been successfully simulated using nonequilibrium molecular dynamics. Steady-state nonequilibrium simulations use "driving" forces to do mechanical work and "constraint" forces to extract the resulting heat. Just as in the Newtonian case, these generalized equations of motion are time-reversible and have constants of the motion associated with them. But, just as in the Newtonian case, the reversibility is illusory. The equilibrium and nonequilibrium equations both exhibit Lyapunov instability, with neighboring phase-space trajectories separating exponentially with time. We describe the methods by treating small systems of two or three particles. Results, for many-body systems, are discussed in terms of a generalized Principle of Corresponding States.
KEYWORDS Nonequilibrium Simulation

I. SCOPE

What problems can we solve with nonequilibrium methods? At a cost of only ten cents for a billion floating point operations, purely academic problems involving up to 10^{15} operations are feasible.[1] I am particularly interested in atomistic problems. I won't discuss solutions of continuum problems or numerical solutions of the Boltzmann Equation. Waves and distribution functions are fine, but for me it is more interesting to see particles move.

Because the particle equations of motion are ordinary differential equations, rather than partial differential equations, both the structure of the equations and the meaning of their solutions are relatively easily understood. Solutions are found by specifying three things:

(i) the initial conditions; the set of particle coordinates and velocities; $\{q, \dot{q}\}$ or $\{q, p\}$;
(ii) the boundary conditions;
(iii) an integration rule, for proceeding from one time to the next.

Methods of numerical integration began to be developed, by Newton, with the discovery of calculus, and are still being improved and refined today. None of the interesting properties of these systems has been shown to be significantly

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influenced by the choice of numerical technique, and so we won't dwell on the various finite-difference approximations to the differential equations here.[2]

Equilibrium systems are either isolated, and not changing with time, or are a part of such an isolated system. Nonequilibrium systems become equilibrium systems unless they are connected to sources of energy.

We can illustrate the essential features of both the equilibrium and the nonequilibrium situations by considering a simple and well-studied[3–7] system, two hard disks, or hard spheres, with periodic boundary conditions. For convenience, we fix the center of mass, so that the two particles move in opposite directions.

At equilibrium, in the absence of external fields, the hard particles travel along straight lines between their elastic collisions. Because the particles are convex, it is clear that eventually the particles will reach any energetically-accessible(non-overlapping) configuration consistent with the fixed center of mass.

It is convenient, particularly in nonequilibrium problems, to study the motion in qp "phase space", in which coordinates $\{q\}$ and momenta $\{p\}$ appear on an equal footing. Thus the two-sphere problem is naturally described in a 12-dimensional phase space. The phase-space dimensionality can be reduced to five(three spatial coordinates and two angles giving the direction of the relative velocity) by considering an equivalent one-body problem and taking conservation of energy into account.

The phase-space trajectories are unstable, from a mathematical point of view. The convex shapes of the colliding particles insure that two initially similar systems rapidly become dissimiliar. Two neighboring trajectories in phase space tend to separate. There is an effective force, linear in the phase-space separation r, for small r, which drives the trajectories apart:

$$\dot{r} = +r/\tau. \tag{1}$$

Thus the separation r grows as $\exp(t/\tau)$. The average value of the "Lyapunov exponent" $1/\tau$ characterizes the rate at which information is destroyed by the equations of motion, or alternatively, the rate at which equilibrium is approached in the absence of dissipation. This trajectory separation can be prevented by adding a generalized "constraint velocity" $\{d\dot{q};\ d\dot{p}\}$ to Hamilton's equations of motion, where the additional velocity is proportional to the phase-space separation of the two trajectories:

$$d\dot{q} = -\Delta q/\tau; \qquad d\dot{p} = -\Delta p/\tau. \tag{2}$$

The magnitude of the velocity is chosen to keep the phase-space separation $(\Delta q^2 + \Delta p^2)^{1/2}$ fixed. The average value of $1/\tau$ can be determined numerically. It depends on the interparticle forces, the temperature, and the density. For hard spheres it is essentially the collision rate. This so-called "chaotic" growth of phase-space separation characterizes both equilibrium and nonequilibrium systems. It is called Lyapunov instability.[8,9]

The simplest way to convert our two-particle equilibrium system to a nonequilibrium one is to add a constant field, accelerating one particle to the right and the other to the left.[3] An average current, proportional to the field, develops, and the phase-space distribution is no longer uniform over the

accessible states. Both particles move faster and faster (getting hotter, from the viewpoint of kinetic theory) as time goes on, by converting potential energy, from the field, into kinetic energy. This heating prevents achieving a steady state. Because steady states are the simplest nonequilibrium states, special methods have been developed for generating them. A frictional force—a "control" or "constraint" force—can be added to keep the kinetic energy constant. The frictional force absorbs the energy as it is provided by the field. The simplest such force would be linear in the momenta $\{p\}$. In general, the additional force could have both parallel and perpendicular components. For a particle moving in the x direction

$$\dot{dp_x} = -\zeta p_x; \qquad \dot{dp_y} = \alpha p_x; \qquad \dot{dp_z} = \beta p_x. \tag{3}$$

The parameter ζ would change the energy of each particle by speeding it up or slowing it down; the parameters α and β would change the direction of the trajectories without changing the speed or energy. So far a useful equilibrium recipe for α and β doesn't exist. If a nice deterministic recipe for them could be found then the equation of motion (3) would be useful for treating Brownian motion and related problems. The Langevin equation could be retired. But Gauss' Principle of Least Constraint[10] requires that the transverse accelerations be zero, providing a unique constraint force. If the magnitude of the driving field becomes large, ζ increases too, in such a way as to keep the kinetic energy constant. In the large-field limit, the particles again travel in straight lines *between* collisions, but the trajectories are parallel to the field. *During* collisions each particle moves along the perimeter of the other in the high-field case.

The two-disk or two-sphere problem contains all the ingredients of a general nonequilibrium simulation problem, with applied, boundary, constraint, and driving forces. In the general case we express the particle accelerations as sums of these four types of forces:

$$m\ddot{r} = F_a + F_b + F_c + F_d. \tag{4}$$

In the two-disk case the interaction between the two disks can be thought of either as an *applied* force F_a, or, for the equivalent one-body problem, as a *boundary* force F_b. The *constraint* force F_c keeps the moving particle(s) at constant temperature(kinetic energy) or at constant energy, whichever is desired. Finally, the *driving* force F_d is responsible for driving the system continuously away from equilibrium. In a thermodynamic analysis of a system with equations of motion of the form (4), "work" is done by the driving force and the corresponding "heat" is extracted by the constraint force.

A two-body or three-body system can provide qualitatively useful results, and aid theoretical developments, but it is too small to be realistic. There is no difficulty in extending the calculations to larger systems. The current world's record for size is the 161,604-particle system studied by Farid Abraham and his coworkers at IBM San José.[10]

In dealing with larger, more realistic systems, driving forces can be used to stimulate flows of mass, momentum, and energy, or they can be generalized to promote defect motion and phase or chemical transformations. This is specially

interesting under far-from-equilibrium extreme conditions, such as those found within shock or detonation waves.

In this short review I will proceed by describing first the simplest systems which can be used to illustrate diffusive, viscous, and heat-conducting flows. These simple cases are treated first because most people find induction more natural than deduction. Then I will describe some results which have been obtained using these techniques, and show how these results have led to useful nonequilibrium generalizations of the Principle of Corresponding States.

II. METHODS

If we study the dynamics of a system of particles confined to a box we will notice a layering of particles parallel to the walls. The distribution is different in a larger system, where the walls are far from most particles. Whenever possible, periodic boundaries should be used to avoid the ordering effects of rigid boundaries. Comparisons between periodic and rigid-boundary simulations show that periodic boundaries minimize the dependence of the results on the number of particles.

If the unit cell of the periodic system doesn't change shape or size with time we can study ordinary diffusion or heat conduction problems. With time-dependent periodic boundaries, deformational flows, viscous flows in fluids and plastic flows in solids, can be studied.

In any of these problems the constraint forces play the role of thermostats. The forces have the form of hydrodynamic frictional forces:

$$F_c = -\zeta p. \tag{5}$$

This form (5) has arisen in a variety of ways:

(i) It is the simplest form suggested by control theory;[12,13]
(ii) If follows from Gauss' Principle of Least Constraint;[10]
(iii) It generates, with the proper choice of ζ, the canonical phase-space distribution of statistical mechanics.[14–16]

To establish (iii) Nosé showed that a friction constant satisfying the relaxation equation

$$\zeta(t) \propto \int^t (K - K_0)\, ds; \tag{6}$$

reproduces the canonical distribution in the absence of driving forces. This was achieved with formally reversible (but still Lyapunov unstable) equations of motion. Although the energy is not conserved with the frictional-force choice (6), a generalized energy, including a heat-bath contribution, *is* conserved. The form of the constant depends also on the driving force F_d. Gauss' Principle leads to a different prescription for ζ (actually a limiting case of Nosé's equations, as the response time of the bath approaches zero):

$$\zeta = -\dot{\Phi}/(2K), \tag{7}$$

where K and Φ are the kinetic and potential energies, respectively. In this case too, the configurational phase-space probability follows the canonical distribution. The deviations from Newton's equations of motion induced by these additional frictional forces are small, of order $1/\sqrt{N}$, and have effects of order only $1/N$ on most properties.

The driving forces entering into the nonequilibrium equations of motion have generally been taken from linear response theory, so that the small-gradient transport coefficients are reproduced in the low-field limit. So far simulations designed to measure the diffusion coefficient,[10] shear and bulk viscosities,[17] and the heat conductivity[18–20] have all been successfully constructed in this way. Several groups have considered the problem of thermal diffusion, but no results are available yet.[21]

Take a definite example. Consider two hard spheres in a periodic box with the center of mass fixed. We add an external field, of strength λ, to stimulate a "current", $\dot{x}_1 - \dot{x}_2$. The equations of motion have the form

$$\dot{x} = p_x/m;\ \dot{y} = p_y/m;\ \dot{z} = p_z/m;$$
$$\dot{p}_x = F_x \pm \lambda - \zeta p_x;\ \dot{p}_y = F_y - \zeta p_y;\ \dot{p}_z = F_z - \zeta_z, \tag{8}$$

with a field $+\lambda$ for Sphere 1 and a field $-\lambda$ for Sphere 2. The constant field λ drives a current, proportional to the x component velocity of either sphere, and the friction coefficient ζ is chosen according to either Gauss' or Nosé's recipe. For Gauss' equations of motion the trajectories can be calculated analytically between collisions.[22] Thus, when the two-body collisions have a random distribution of impact parameters, this low-density two-body problem can be solved. The solution leads to a diffusion coefficient which decreases with increasing field strength. For two disks, the diffusion coefficient is about 25% higher than the value found for an infinite system of disks by solving the Boltzmann equation.[7]

The equations of motion in a shear flow for two hard disks, or spheres, are very similar. Again the transport coefficient decreases with increasing field, this time from a zero-field value about the half the thermodynamic limiting value.[4,6]

For heat flow, the situation is a little more complicated.[23] To maintain consistency with irreversible thermodynamics, the equations of motion have a driving force depending upon the energies of the particles and their contributions to the potential part of the pressure tensor P^{Φ}:

$$F_d = \lambda[E - \langle E\rangle + P^{\Phi}_{xx}V - \langle P^{\Phi}_{xx}V\rangle,\ P^{\Phi}_{xy}V - \langle P^{\Phi}_{xy}V\rangle,\ P^{\Phi}_{xz}V - \langle P^{\Phi}_{xz}V\rangle]. \tag{9}$$

In the two-particle case all of these forces vanish, because both particles have the same (average) energy and potential pressure tensor contributions. $\langle E\rangle$ and $\langle P^{\Phi}\rangle$. Thus, for two particles, the heat current is zero.[16]

It is therefore necessary to use three particles to study heat flow. This has recently been done, for hard disks and hard spheres,[23] and the conductivities lie considerably farther below the large-system limit than do the viscosities. Again, the transport coefficient shows a decrease with increasing field strength.

In most nonequilibrium simulations, and all of these described here, the equations of motion are time-reversible, so that a movie of the motion, run

backwards, would obey exactly the same equations of motion. But the information loss inherent in Lyapunov instability makes the reversibility impossible in principle. Despite their formal reversibility, the solutions display an irreversible nature. This is fortunate, because *true* reversibility of the equations would imply that the transport coefficients all vanish.

These few-particle systems are ideal for studying the application of new methods to equilibrium and nonequilibrium systems. The partition functions and dynamics for these small systems can be treated analytically and sometimes offer hints as to simplifications useful for larger systems.

III. RESULTS

For simple diffusion, viscosity, and conduction, there is no difficulty, beyond the computer time involved, in obtaining accurate data. The results are consistent from one investigator to another, and also agree with experiment in cases where the forces can be estimated. The accuracy of the results depends on the time (errors varying as the inverse square root of time) and number of particles (errors varying as $1/N$). It is good practice to arrange that these two sources of error be roughly equal.

The results from nonequilibrium simulations can be related to equilibrium properties in many ways. Eventually a useful predictive scheme will emerge. It appears that *entropy* is a particularly good choice of thermodynamic variable to correlate with transport properties.[24] Entropy measures the states available, and these available states should be correlated with the mean free path, collision frequency, and other ingredients of approximate theories of transport.

It is convenient to measure the entropy relative to that of an ideal gas, in which no correlations are present so that the maximum number of states is available. Thus, the excess entropy is always negative, and reaches about $-6Nk$ at the freezing line. If we follow Rosenfeld's lead in plotting logarithms of reduced transport coefficients (diffusivities, conductivities, and viscosities) from fluid simulations versus excess entropy, nice straight lines are found, in every case. For reduction purposes, the transport coefficients are made dimensionless using appropriate combinations of the molar volume and mass, the temperature, and Boltzmann's constant. Typical deviations from these straight lines are roughly 15%, 20%, and 10% for diffusion, shear viscosity, and thermal conductivity.

On the basis of simple Einstein-model ideas, one might expect that the slopes of these straight lines would be $-1/3$ for reduced diffusion coefficient and $+1/3$ for reduced viscosity and conductivity, when plotted versus $-S^e/Nk$. The connections are these, all expressed in terms of the Einstein frequency ν. The mean free path, which determines the diffusion coefficient should vary inversely as ν. The collision rate, which determines momentum and energy transport, should vary directly as ν. Finally, the entropy, which varies as the logarithm of the canonical partition function

$$Z_{\text{canonical}} \sim (kT/h\nu)^{3N}, \tag{10}$$

varies as *three* times the logarithm of ν. A more careful attempt to draw tl correlation, keeping track of the additive and multiplicative constants, looks ve promising, on paper. Unfortunately, the slopes for diffusion and viscosity a quite far from the Einstein-model prediction. The agreement for heat condu tivity is not bad. In any event, the straight lines found by correlating compute generated transport coefficients have proved useful in making reliable estimat for real fluids in a range of temperatures and densities where no accurate theo exists.

A similar kind of Corresponding States Principle holds for the yield strength c solids, which has been measured as a function of strain rate and temperature fc both two and three-dimensional solids.[25] Again the correlation was foun empirically, by studying the results of shear simulations in which the strain rate was applied to solids rather than fluids. In either case, fluid or solid, the equation of motion are:

$$\begin{aligned} \dot{x} &= (p_x/m) + \dot{\varepsilon}y; & \dot{p}_x &= F_x - \dot{\varepsilon}py - \zeta p_x; \\ \dot{y} &= (p_y/m); & \dot{p}_y &= F_y - \zeta p_y; \\ \dot{z} &= (p_z/m); & \dot{p}_z &= F_z - \zeta p_z, \end{aligned} \tag{11}$$

where $\dot{\varepsilon}$ is the macroscopic hydrodynamic derivative of the x velocity with respec to y ($\dot{\varepsilon}$ is just a constant during the molecular dynamics simulation, but its valu determines the rate at which the periodic boundaries deform.) The friction coefficient ζ can again be selected according to either Gauss' or Nosé's recipe. Then solids can be sheared.

If this is done, an initially perfect crystal typically reacts by generating a pair o dislocations at a shear strain on the order of a few percent. The shear stress drops and the dislocations separate at a high, but subsonic, velocity. If the strain rate is larger, *many* dislocations can be observed. Crystals typically saturate with dislocations at strain rates of 10^{13} hertz or so, corresponding to the relative motion, at the velocity of sound, of neighboring atoms in the deforming crystal. The vast range of yield strengths and strain rates again suggests a logarithmic corresponding-states plot. If the stresses are reduced by the shear modulus and the strain rates by the product of the sound speed and the inverse of the interparticle spacing, a nice straight-line correlation again results, with the slope increasing linearly with temperature. These extrapolated straight lines, based on computer simulations at 10^9 to 10^{12} hertz, agree reasonably well with experimental yield strengths, now available at strain rates up to about 10^6 hertz.

The availability of these new simulation techniques for simulating states far from equilibrium should make it possible to improve cell models in a systematic way. The prospects for treating coupled transport processes are also good. By taming the Lyapunov instability, it is possible that more convincing results can be obtained from response theory.[26] In addition, the analytic solutions becoming available for some of these same nonlinear problems should lead to progress in developing a theoretical approach to dense-fluid transport. It is now an exciting time for nonequilibrium simulation.[27]

NOMENCLATURE

dp	momentum constraint
dp_x	momentum constraint component
dp_y	momentum constraint component
dp_z	momentum constraint component
dq	coordinate constraint
ds	time differential
E	particle energy
F_a	applied force
F_b	boundary force
F_c	constraint force
F_d	driving force
F_x	force component
F_y	force component
F_z	force component
h	Planck's constant
K	kinetic energy
K_0	fixed kinetic energy
m	mass
N	number of particles
p	momentum
p_x	momentum component
$\dot{p}_x$	acceleration component
p_y	momentum component
$\dot{p}_y$	acceleration component
p_z	momentum component
$\dot{p}_z$	acceleration component
P^Φ	potential pressure tensor
P^Φ_{xx}	potential pressure component
P^Φ_{xy}	potential pressure component
P^Φ_{xz}	potential pressure component
P^Φ_{yy}	potential pressure component
P^Φ_{yz}	potential pressure component
P^Φ_{zz}	potential pressure component
q	coordinate
$\dot{q}$	velocity
r	phase-space location

$\dot{r}$ phase-space velocity
$\ddot{r}$ acceleration
S^e Excess entropy
t time
T temperature
V total volume
$\dot{x}$ velocity component
$\dot{y}$ velocity component
$\dot{z}$ velocity component
Z canonical partition function

Greek Letters

α Lagrange multiplier
β Lagrange multiplier
Δp momentum separation
Δq coordinate separation
$\dot{\varepsilon}$ strain rate
ζ Nosé friction coefficient
λ field strength
ν Einstein frequency
τ Lyapunov time
Φ potential energy
$\dot{\Phi}$ potential power
$\langle\ \rangle$ Instantaneous average

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