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Non-equilibrium simulations

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Particle methods can be used in non-equilibrium simulations of both microscopic atomistic flows and macroscopic hydrodynamic flows. In the microscopic case, many-body systems can be driven away from equilibrium, into non-equilibrium states, by adding boundary, constraint, or driving forces to the usual atomistic forces:

$$m\ddot{r}_{\text{NEMD}} \equiv \dot{p} \equiv F_A + F_B + F_C + F_D.$$

The additional forces can act as energy sources and sinks, with which the driven system can exchange heat, and through which it can perform mechanical work. In adapting similar 'smoothed-particle' methods to macroscopic problems, moving boundaries and heat reservoirs can be treated more easily, simply by specifying the velocities and temperatures of special boundary particles. The smoothed-particle technique suggests a natural form of turbulent eddy viscosity which damps the shortest-wavelength hydrodynamic velocity fluctuations.

Here, 25 years of development of non-equilibrium particle methods are highlighted, emphasizing the importance of thermostats and boundary conditions to this activity, and illustrating microscopic fractal phase-space distributions and the simulation of macroscopic hydrodynamic instabilities with recent worked-out examples. Some remaining puzzles are given which we hope will be solved in the near-term future.

1. Introduction

In 1976 [1], Doug Henderson and John Barker asked the question 'What is liquid?'. Up to that time, and despite Gibbs' exact theory, the structural and thermodynamic properties of dense fluids had seemed mysterious. Neutron and X-ray scattering experiments provided only a tantalizing two-body indication of the underlying many-body liquid structure. *Ad hoc* integral equations and cell models were providing crude estimates for comparison with the more reliable results of computer simulations. In 1976 computers were still so slow that 500 particles represented a 'big' system. At the time of Barker and Henderson's 1976 review, our understanding of equilibrium properties had just improved, qualitatively. With reference-system pair-correlation structures taken from computer simulations, thermodynamic perturbation theory made it possible to compute, within a per cent or so in favourable cases, equilibrium energies and pressures throughout a perturbed-system phase diagram. Doug Henderson played an important role in making and exploiting this advance.

Twenty years later our understanding of liquids is again undergoing rapid change, this time in response to increases in computer speed and capacity. Massively parallel simulations with millions [2], or even billions [3], of degrees of freedom are becoming

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routine. Trillions lurk just beyond the teraflop horizon [4]. The 1976 goals of generating phase diagrams and equilibrium properties for simple potentials can now be achieved with a few minutes work on a fast work station. Where is the presentday challenge for simulation and for statistical mechanics? We believe that it lies in understanding *non-equilibrium* systems, particularly those which exhibit macroscopic Lyapunov instability. Such dissipative mechanical systems always involve heat and work, and usually require the judicious consideration of thermodynamic processes together with a description of the boundaries between a system and its surroundings.

In discussing presentday non-equilibrium algorithms, we recall the goals that Zwanzig emphasized in Mexico, as reported in Kinam in 1981 [5]. He pointed to the importance of calculation, or simulation, in advancing theory. He also identified four major goals: understanding (i) the approach to equilibrium, (ii) non-equilibrium steady states, (iii) metastability, and (iv) kinetic equations. With the passage of time, our goals today are a little different, though simulation remains the most reliable route to new knowledge in non-equilibrium problems.

As to Zwanzig's first goal, we are today hardly closer than was Boltzmann, a century ago, when he proved the H theorem. For most physicists, that is close enough; it is not at all clear what would constitute a further advance towards this goal. By 1956 Alder and Wainwright had shown, numerically, that the H theorem describes the *averaged* approach to equilibrium [6], omitting the number-dependent fluctuations about the average, which remind us of Poincaré's and Liouville's theorems.

Simulation has clarified our understanding of non-equilibrium steady states [7], Zwanzig's second goal, in several ways: we have learned how to achieve these states with special constraint and driving forces which caricature the mechanical and thermal interactions of a system with its surroundings; we have learned that the phase-space distributions associated with these non-equilibrium stationary states are typically multifractal; we have also learned that nonlinear deviations from equilibrium are rarely very large. Generally speaking, physicists are satisfied with our understanding of goals one and two.

We widen Zwanzig's third goal, understanding metastability (as in quiescent supercooled liquids), to include an understanding and the simulation of *dynamic* instabilities and turbulent flows. It has become recognized that the 'Lyapunov instability', with perturbations growing as $\exp(\lambda t)$, is pervasive in both microscopic and macroscopic dynamics [7–9]. The ability of numerical methods to predict and to reproduce these instabilities promises to be a valuable guide to the future development of efficient simulation algorithms. Much remains to be done.

Zwanzig's fourth goal, developing kinetic equations, is gradually falling by the wayside, and is becoming replaced by the goal of non-equilibrium algorithmic development, as rapid and low-cost simulations replace the complex theoretical approaches and structures of the sliderule era.

In the present review we emphasize W.G.H.'s research interests and recent work, mainly as devoted to forging a parallel link between microscopic and macroscopic non-equilibrium systems. Our understanding has followed the route suggested by Zwanzig's analysis, from steady states to instabilities, through new microscale equations of motion. The present authors have collaborated recently in the smoothed-particle work.

2. Molecular dynamics and smoothed particle applied mechanics

The two simulation methods we consider here are non-equilibrium molecular dynamics (NEMD) [7, 9, 10], augmenting Newton's equations of motion,

$$m\ddot{r}_{\text{Newton}} \equiv \dot{p} \equiv \sum (-\nabla_i \phi_{ij}) = F_{\text{A}},$$

with boundary, constraint, and driving forces,

$$m\ddot{r}_{\text{NEHD}} \equiv \dot{p} \equiv F_{\text{A}} + F_{\text{B}} + F_{\text{C}} + F_{\text{D}},$$

and smoothed-particle applied mechanics (SPAM) [11–14] in which mesoscopic continuum particles are smeared out, using a normalized density $w(r)$, so that each particle's continuum-based equation of motion involves a weighted average of local stresses:

$$\{\ddot{r}_{\text{SPAM}} \equiv \dot{v} \equiv \sum [(\sigma/\rho^2)_i + (\sigma/\rho^2)_j] \cdot \nabla_i w_{ij};\ \rho_i \equiv \sum w_{ij}\};\quad \int_0^l 2\pi r w \, \mathrm{d}r \equiv 1.$$

In both cases, microscopic NEMD and macroscopic SPAM, we will here choose all the particle masses $\{m\}$ equal to unity, for simplicity.

Both computational methods can be applied to non-equilibrium simulations. Newton's, Lagrange's, or Hamilton's microscopic motion equations provide forces which depend upon the coordinates $\{q\}$; these forces are the conventional sources and sinks for thermodynamic work. But these mechanical equations of motion do not contain sources or sinks of heat, which must be defined in terms of the momenta $\{p\}$ through the ideal-gas temperature scale $kT \equiv \langle p^2/m \rangle$. Thus non-equilibrium molecular dynamics is an extension of classical mechanics which includes the study of heat sources and sinks, as described by constraint and driving forces [7, 9, 10].

Macroscopic hydrodynamics, in the form of bulk conservation equations for mass, momentum, and energy, also needs to be augmented, at least with boundary conditions, and perhaps also with energy sources and sinks. The details of the hydrodynamic boundary conditions depend upon the solution method, i.e., finite differences, finite elements, or smoothed particles. Because the hydrodynamic equations typically incorporate constitutive relations which proceed irreversibly towards a maximum entropy state, any understanding of flows which include spontaneous thermal fluctuations requires an explicit treatment of source terms to offset the continual damping provided by viscosity and heat conduction. How should these thermal fluctuations be included? We discuss some general aspects of generating and interpreting these Lyapunov-unstable fluctuations in sections 3 and 4. Applications are described next, in sections 5 and 6. These are followed in section 7 by a list of problems well suited to investigation in the near future. In response to an editorial request we add, as section 8, a brief summary of our view of irreversibility in statistical mechanics.

3. The nature of microscopic irreversible flows from NEMD

Microscopic irreversible flows must be driven by non-equilibrium equations of motion which incorporate the effects of thermostats, or ergostats, which in turn exchange energy with the system of interest. Heat exchange can be time-reversible (Gauss or Nosé–Hoover) or irreversible (Berendsen or Langevin), as well as deterministic or stochastic. We will discuss here only the reversible-deterministic

combination, for this choice simplifies the phase-space analysis of non-equilibrium systems, and extends the conclusions which can be drawn from these analyses.

The mechanical basis of Gibbs' equilibrium statistical mechanics is Liouville's theorem, which describes the constant-phase-volume flow of probability density for the fluid through phase space which occurs in systems lacking a mechanism for heat exchange with their surroundings. Heat exchange makes a fundamental difference: with it the comoving phase volume $\otimes$ can expand or contract in response to time-reversible heat transfers. The phase-space probability density f also varies, in just such a way that the product, $\otimes f$, is constant, following the flow. As a consequence, characteristic of steady irreversible flows, and tied closely to their Lyapunov-unstable nature, the phase space attractors representing non-equilibrium steady states are *multifractal* objects. Liouville's theorem for equilibrium systems, $\mathrm{d}\ln f/\mathrm{d}t \equiv 0 \equiv -\mathrm{d}\ln \otimes /\mathrm{d}t$, is generalized, in this case, to read

$$\mathrm{d}\ln f/\mathrm{d}t_{\mathrm{NEMD}} \equiv -d\ln \otimes /\mathrm{d}t = \sum \zeta_T = \sum -\lambda_{\mathrm{Local}} = -\sum (\dot{Q}/T)_{\mathrm{In}} - \sum (\dot{Q}/T)_{\mathrm{Out}}.$$

$\dot{Q}$ is positive for heat flowing into, and negative for heat flowing out of, the system. Here, $\{\lambda_{\mathrm{Local}}\}$ represent the local comoving corotating rates of expansion and contraction (a pair of these 'Lyapunov exponents' for each mechanical degree of freedom). Mechanical stability requires that the time-averaged friction-coefficient sum $\langle \sum \zeta_T \rangle$ be positive, and that the time-averaged Lyapunov-exponent sum $\sum \lambda \equiv \langle \sum \lambda_{\mathrm{Local}} \rangle$ be negative. Otherwise the occupied phase volume $\otimes$ would grow without bound. Individual terms in all of these sums can be positive, zero, or negative. For instance, in the flow of heat from a hot boundary to a cold one, the time-averaged heat extracted at the cold boundary, $\langle (\dot{Q})_{\mathrm{Out}} \rangle = \langle -(\dot{Q})_{\mathrm{In}} \rangle$, is negative.

The inexorable loss of phase-space volume, required for steady-state stability, leads to a fractal phase-space attractor, with (information) dimension strictly less than the equilibrium value. The zero-phase-volume attractor, although described by time-reversible dynamics, is made up of states which are negligibly improbable at equilibrium. When time-reversed, these attractor states make up a repellor which is even more unstable and on which the transport coefficients are negative. The overwhelming stability of the attractor ($\sum \lambda < 0$), relative both to the equilibrium states ($\sum \lambda \equiv 0$) and to the repellor states ($\sum \lambda > 0$), is the microscopic mechanical analogue of the Second Law of Thermodynamics [15].

The attractor dimensionality (equal to the repellor dimensionality) can be estimated from the Lyapunov spectrum. Sums of $\{1, 2, 3, \ldots\}$ Lyapunov exponents $\{\lambda\}$ measure the growth rates of $\{1, 2, 3, \ldots\}$-dimensional objects, so that, for instance, the growth rate of an infinitesimal phase-space sphere is given by the sum $\lambda_1 + \lambda_2 + \lambda_3 \equiv \langle \mathrm{d}\ln V_{3\mathrm{D}}/\mathrm{d}t \rangle$. Thus, by finding the dimensionality for which the growth rate $\sum' \lambda$ of a comoving phase-space hypervolume of reduced dimensionality is exactly zero, it is possible to determine the precise (Kaplan–Yorke) dimensionality of the steady-state strange attractors which exhibit no volume change with time. Recent work strongly suggests that this non-equilibrium loss in dimensionality, $\Delta D \equiv D_{\mathrm{Equilibrium}} - D_{\mathrm{KY}}$ is extensive [16], persisting in the large-system 'hydrodynamic limit', and varying as the square of the deviation from equilibrium [9].

4. The nature of macroscopic irreversible flows

The evolution equations for a continuum,

$$\mathrm{d}\ln \rho/\mathrm{d}t = -\nabla \cdot v;\ \mathrm{d}v/\mathrm{d}t \equiv (1/\rho)\nabla \cdot \sigma;\ \mathrm{d}e/\mathrm{d}t \equiv (1/\rho)[\nabla v : \sigma - \nabla \cdot Q],$$

require constitutive relations giving the stress σ and the heat-flux vector Q in terms of $\rho(r, t)$, $v(r, t)$, and $e(r, t)$. Irreversible macroscopic flows are described by dissipative constitutive equations, which typically include plasticity, or Newtonian viscosity, as well as Fourier heat conduction. These dissipative processes inexorably diminish velocity and temperature differences. The most interesting systems can be driven into wild chaotic time variation despite fixed non-equilibrium boundary conditions. For fluids, turbulence is the generic example.

How does macroscopic turbulence differ from microscopic chaos? Turbulence is intrinsically a non-equilibrium property while microscopic chaos is much the same at, or away from, equilibrium. In fact, numerical techniques which incorporate macroscopic fluctuations exhibit Lyapunov spectra for microscopic and macroscopic systems which look very much alike [9, 14]. Nevertheless, there certainly is an intrinsic qualitative difference between the perpetual conservative motion of a Hamiltonian system, or a system constrained and driven by time-reversible thermostatting forces, and the damped motion described by the Navier–Stokes equations.

The Russian literature [17] stresses the need for phenomenological source terms in describing hydrodynamic flows with fluctuations. One way these can be modelled is by following Nosé's thermostat idea [7, 18–20], providing energy to the system with feedback. Energy sinks are often included to stabilize hydrodynamic simulations of shockwaves (with 'artificial viscosity'), and to avoid the explicit consideration of short wavelength degrees of freedom (with 'eddy viscosity'). Smoothed-particle applied mechanics contains natural velocity fluctuations, with two different estimates of the velocities at the nodal points; $\{v\}$, the velocities at which the points move, and the spatially averaged velocities $\{\langle v\rangle\}$ characterizing the neighbourhood of each moving point. In the absence of damping, smoothed-particle applied mechanics, like Newtonian mechanics, is exactly time-reversible. If damping is required, as in driven systems, then the difference between the two point velocities provides a natural high-frequency short wavelength heat sink:

$$\dot{v}_{\text{EDDY}}^{\text{SPAM}} \equiv [\langle v\rangle - v]/\tau,$$

where τ is a phenomenological relaxation time which can be used to control the system energy.

Boundaries are the crucial link between the system of interest and the surroundings with which it interacts. In particle methods the effects of boundaries must occur in the equations of motion of the particles $\{\dot{r}, \dot{v}, \dot{e}\}$. In the smoothed-particle case we have used two natural ways for treating system boundaries. Sufficiently many particles fixed in space can be used, to provide a high-density container region capable of repelling approaching particles. It is equally simple to use a mirror boundary condition in which approaching particles are reflected (see figures 1 and 2). An advantage of the smoothed particle approach is that the velocities and temperatures of the reflected boundary particles can be assigned independent of other particles in their vicinity, even the mirror-image particles inside the system.

5. Microscopic examples using NEMD

The general nature of non-equilibrium steady states was made clear first through the study of two simple one-body problems [10, 21–24]. The field-driven motion of a hard disc through a fixed lattice of similar discs [22, 23], with the motion constrained to occur at fixed kinetic energy, provides a simple model for conductivity.

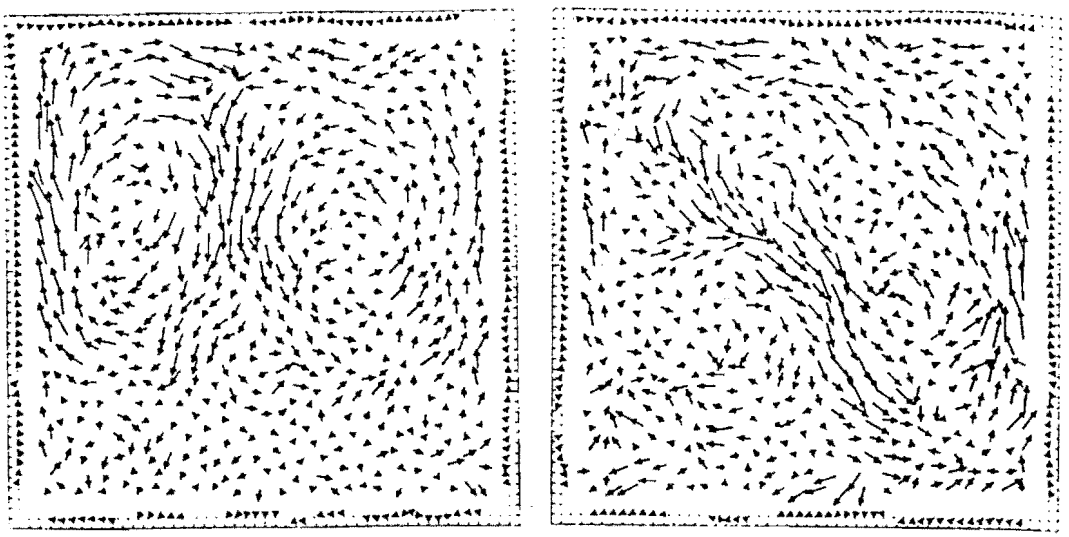

Figure 1. Rayleigh–Bénard simulation using 200 fixed smoothed particles, to form horizontal and vertical boundaries, along with 576 moving particles in the bulk fluid. Heat is transferred from the bottom to the top in the presence of a vertical gravitational field.

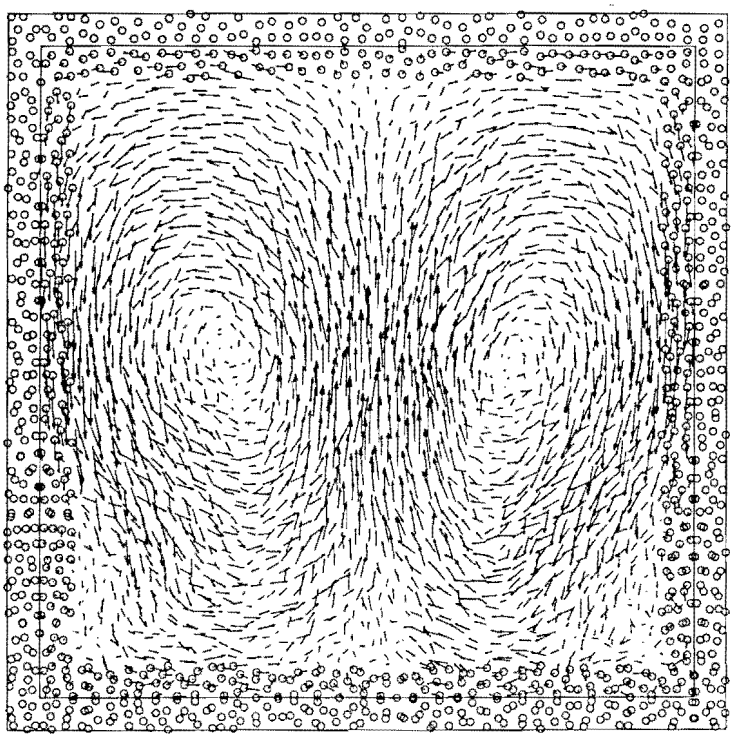

Figure 2. Rayleigh–Bénard simulation using 2500 smoothed particles. The boundaries are mirrors. The boundary particles (open circles), which have specified velocities and temperatures, are reflected images of interior particles (open circles with velocity arrows), which obey the bulk equations for momentum and energy transport.

The ergodic phase-space mixing of the hard-disc system is a good model for more complicated many-body systems. A shearing lattice of hard discs, again with a scatterer moving at fixed kinetic energy relative to the mean flow, provides the simplest model of viscous flow [10, 24].

In both hard-disc cases, diffusion and shear, it is possible to carry out detailed statistical studies by studying millions [or billions!] of successive collisions. Because hard-disc collisions are characterized by just two variables, angles giving the location and the direction of motion after each collision, the phase-space distribution function can be constructed from the distribution of collision angle pairs $\{\alpha, \beta\}$. Figure 3 indicates the development of the fractal nature of that distribution starting from the uniform equilibrium distribution.

For shear flow an additional periodic strain variable is required. The numerical data show that both these simple steady non-equilibrium diffusive and shearing states generate multifractal phase-space distributions. These have zero measure, relative to the equilibrium measure of the space, showing that despite the time-reversible nature of the equations of motion, the non-equilibrium states form a set of zero measure. Application of Liouville's theorem to the equations of motion establishes that the comoving phase volume approaches zero almost everywhere, and that the probability density diverges to infinity, in both of these systems [15, 16]:

$$[\langle \mathrm{d} \ln f/\mathrm{d}t_{\mathrm{NEMD}} \equiv -\mathrm{d} \ln \otimes /\mathrm{d}t\rangle] > 0 \Rightarrow \{f \Rightarrow +\infty; \otimes \Rightarrow 0\}.$$

Exactly these same relations hold in a many-body non-equilibrium system. We have just completed a study of two-dimensional steady shear flows [25, 26]. Besides showing that the phase-space dimensionality loss is 'extensive', proportional to

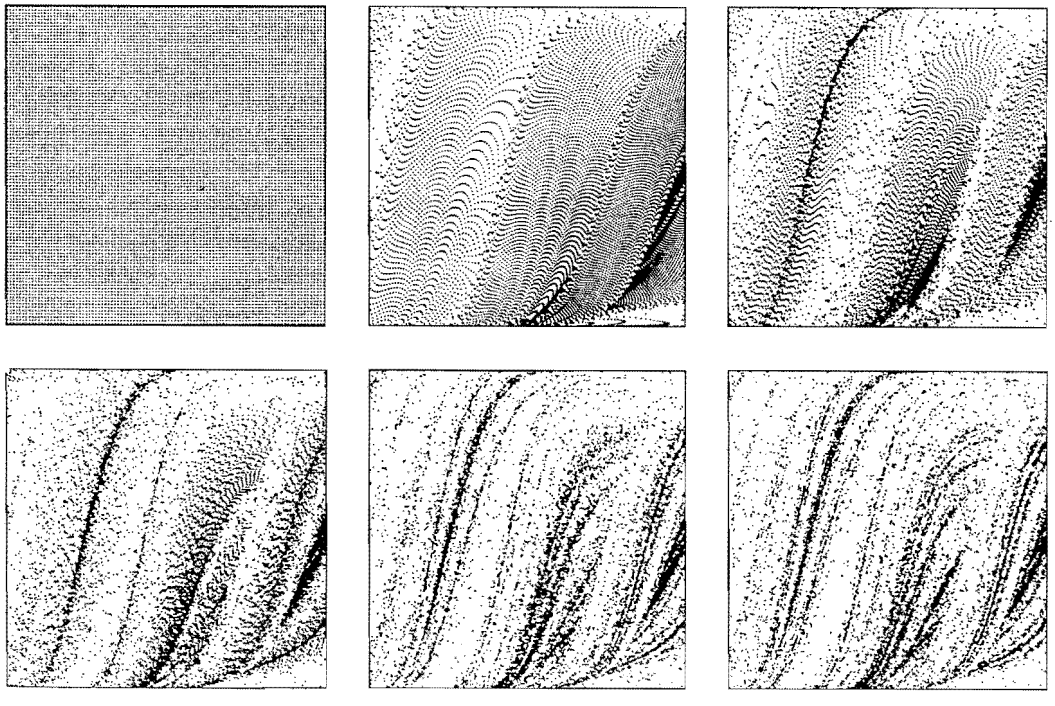

Figure 3. Time development of the multifractal phase-space attractor for the diffusive hard-disc problem, showing the collisions $\{\alpha, \sin \beta\}$ for a set of 10 000 hard discs after 1, 2, 3, 5 and 10 collisions.

system size, the data established that the viscosity in two dimensions is well behaved, for a fixed value of the strain rate, showing no trace of the large-system divergence predicted by mode-coupling and kinetic theories. This unexpected result makes it possible to define a hydrodynamic limit, for shear flows, analogous to the equilibrium thermodynamic limit. No similar result has been obtained for heat flows. It appears that the Evans homogeneous heat-flow algorithm is unstable for large two-dimensional systems and may well also fail in three dimensions [25].

6. Macroscopic analogues of microscopic flows, using SPAM

SPAM provides an interesting bridge between continuum mechanics and molecular dynamics, for the particles in SPAM can represent any desired quantity of material. A semiquantitative simulation of Rayleigh–Bénard instability, which typically requires many thousands of particles in molecular dynamics simulations [27], can be carried out with only a few hundred particles. See again figure 1 for a snapshot of such a flow.

There is an extremely interesting relationship between the Newtonian equations of motion for a dense fluid and the smoothed-particle equations for a particular ideal gas [14]. If the two-dimensional monatomic ideal-gas equation of state $P = \rho^2/2$ is chosen, then the smoothed-particle equations, and the trajectories they generate, are *isomorphic* with the equations of molecular dynamics, using the *weighting* function $w(r) \equiv \phi(r)$ as a *potential* function:

$$\{\ddot{r}^{\text{Ideal}}_{\text{SPAM}} \equiv \sum(-\nabla_i w_{ij}) \equiv \sum(-\nabla_i \phi_{ij}) \equiv \ddot{r}_{\text{MD}}\}.$$

This isomorphism appears both peculiar and paradoxical, because the molecular dynamics motion, from $\phi(r)$, although conservative and perpetual, must certainly exhibit the long-wavelength viscous dissipation and heat conduction associated with irreversibility. At the same time, the Eulerian motion, obtained from $w(r)$, following the equations of fluid mechanics, containing no explicit dissipation, and, applied to an isentropic ideal gas, can exhibit only a Reynolds stress viscosity but no true irreversibility.

We sought to understand the isomorphism better by measuring the 'shear viscosity' associated with the smoothed-particle version of a two-dimensional ideal gas. We used Lucy's weighting function with a range of 3 and at unit density, corresponding to ordinary NEMD with a pair potential:

$$w(r) = \phi(r) = (5/9\pi)[1 + r][1 - (r/3)]^3 \quad \text{for } r < 3.$$

The NEMD equations of motion include the strain rate $\dot{\epsilon} \equiv \mathrm{d}u_x/\mathrm{d}y$:

$$\dot{x} = (p_x/m) + \dot{\epsilon}y; \qquad \dot{p}_x = F_x - \dot{\epsilon}p_y - \zeta p_x;$$

$$\dot{y} = (p_y/m); \; \dot{p}_y = F_y - \zeta p_y; \qquad \zeta \equiv -\dot{\epsilon}P_{xy}V/2K.$$

The shear stress $-P_{xy}$, at strain rates of 0·25, 0·50, and 1·00, and with a fixed internal energy of $E \equiv \Phi + K \equiv N/2$, was always approximately 0·03, for systems of from 64 to 576 particles. The lack of an approximately linear dependence of stress on strain rate suggests that the w fluid can provide interesting non-Newtonian flows resembling those of a plastic material with yield stress 0·03.

To put the relatively tiny magnitude of this rate-independent shear stress in context we computed the w solid's shear modulus, for the two-dimensional static

triangular lattice. At unit density, this lattice has a slightly lower energy per particle than does the square lattice. The lattice sums of $\phi(r)$, including $\phi(0) = (5/9\pi) = 0{\cdot}17684$, are

$$\sum_{\text{Triangular}} \phi(r) = 1{\cdot}00223; \quad \sum_{\text{Square}} \phi(r) = 1{\cdot}00293,$$

showing that the smoothed-particle approach reproduces the mean density with an error of less than half a per cent. The two-dimensional shear moduli, $G \equiv \sigma_{xy}/\epsilon_{xy}$, are given by the expressions [28]:

$$GV \equiv \sum_{\text{Pairs}} (x^2y^2/r^4)(r^2\phi'' - r\phi') - PV; \quad PV \equiv -\sum_{\text{Pairs}} (y^2/r^2)r\phi',$$

and have the numerical values 0·0071 and 0·0052 for the triangular and square lattices, respectively. Thus the measured stress, though negligible with respect to the ideal-gas bulk modulus, $B_S \equiv \rho(\partial P/\partial\rho)_S \equiv 2P \equiv 2E/V \equiv 1$, is substantially greater than the shear modulus.

We expect to explore further the constitutive properties of the smoothed-particle weighting function, viewed as a pair potential, in order to clarify the usefulness of the smoothed-particle approach to the modelling of high-Reynolds-number flows. The exact analogy between the smoothed-particle hydrodynamic equations and molecular dynamics has another striking aspect: Levesque and Verlet [29] have proved that the common leapfrog algorithm can provide bit-perfect time-reversibility in equilibrium molecular dynamics. We have shown [14] that their idea can be extended to the Euler equations, as might be expected on the basis of this isomorphism.

7. Problems for the near-term future

Because the methods discussed here are still relatively new, with some versions and variations being invented independently by several workers, a contentious and confusing literature has developed, in which both justified and unjustified claims are made for one or another of the various approaches. The uncritical acceptance of such claims is a calculated risk the beginner should attempt to avoid. With this warning in mind, what progress can we expect to see in the next few years?

Klimontovich [17] has raised an important subject in his text, the analysis of the enhanced effect of mesoscopic fluctuations on transport coefficients. Fluctuations have been a part of equilibrium statistical mechanics for 50 years, because their decay is directly related to linear transport through the Green–Kubo relations. But it is only recently that non-equilibrium fluctuations (turbulence) have been tractable for quantitative numerical studies in three space dimensions.

It seems to us highly likely that both the rumoured logarithmic divergence of two-dimensional transport coefficients and the order-unity centre-of-mass contribution to the Reynolds number, in two dimensions, are direct consequences of fluctuations. It is certainly hopeless to claim to understand three-dimensional turbulence without first achieving a firm understanding of fluctuations in two dimensions.

Klimontovich also attempts to analyse the convergence of microscopic dynamic simulations to macroscopic continuum mechanics. He combines diffusive [$dt < dx^2/D$] and sound [$dt < dx/c$] constraints on the timestep dt with a timestep based on the mesoscopic collision rate. Though his results are odd and his estimates seem to be

unduly pessimistic, it would be profitable to follow up his ideas with the aid of accompanying simulations.

It was suggested long ago [30] that 'long-time tails', of the Green–Kubo correlation functions, are related to the difference in the Eulerian and Lagrangian forms of the diffusion equation,

$$(\partial\rho/\partial t)_{\text{Euler}} = D\nabla^2\rho;\ (\mathrm{d}\rho/\mathrm{d}t)_{\text{Lagrange}} = D\nabla^2\rho.$$

Here again the two-dimensional fluctuations, in the location of the measurement device relative to the fluid being measured, affect the transport coefficients $\{D\}$. This too requires more study in two dimensions. The special interest of these two-dimensional problems is enhanced by the relative simplicity of two-dimensional computer graphics.

Extending Liouville's theorem to smoothed-particle applied mechanics, and possibly to hybrid models, combining both microscopic NEMD and macroscopic SPAM, can provide information over a wide range of dissipative scales, linking fluctuation and instability studies together. The result of these investigations will be a close coupling between large and small scale phenomena, enriching both types of simulation, particularly those seeking a better understanding of fracture and of turbulence.

8. Irreversibility in statistical mechanics

Before the computer revolution the development of equilibrium statistical mechanics was mainly analytic. In this development it was natural to use Hamiltonian mechanics and to emphasize 'infinite systems', systems without the boundaries which complicate analytic work. In some restricted cases it could even be demonstrated that the free energies of N body systems approach a well defined large-system 'thermodynamic limit' with the free energies proportional to N. The success of Gibbs' statistical mechanics has since led many workers to emphasize the study of purely-Hamiltonian non-equilibrium systems, again with infinitely many degrees of freedom.

To us, this approach appears to be a dead end. Real non-equilibrium systems are driven systems, with sources, sinks, and boundaries. As Lebowitz has repeatedly emphasized, it is difficult to improve upon Boltzmann's understanding of irreversibility so long as one ignores these features and studies only large isolated Hamiltonian systems. On the other hand, the chaotic mixing character of very small systems, as evidenced in the figures, together with the development of time-reversible thermostats (based on the ideal-gas thermometer), following up Nosé's discovery, made it possible to generalize Hamiltonian mechanics to include time-reversible deterministic boundary forces modelling sources and sinks of thermodynamic work and heat. This generalization of classical mechanics has three very real advantages:

(i) The number of degrees of freedom is reduced; one can study far-from-equilibrium systems with only a few degrees of freedom. This facilitates computation, simulation, visualization, analysis, and, as Zwanzig emphasized, understanding.

(ii) The visualization, analysis, and understanding of *irreversibility* is, in particular, made much simpler. The Lyapunov instability of the few-body equations of motion, coupled to Nosé's time-reversible thermostats, makes it possible to

prove that the time development of these flows satisfies the macroscopic Second Law of Thermodynamics.

(iii) The resulting links between microscopic and macroscopic simulations have enhanced our understanding of both approaches.

This new approach to understanding required computers. We believe that it will seem as natural to the students of tomorrow as the study of infinite Hamiltonian systems was to the students of yesterday.

One of us (W.G.H.) very much appreciates this opportunity to help honour Douglas Henderson, on the occasion of his sixtieth birthday. The work described here was supported by (i) the Lawrence Livermore National Laboratory, under the auspices of the United States Department of Energy, through Contract W-7405-Eng-48, (ii) the Academy of Applied Science (Concord, New Hampshire), (iii) the Agency for Defense Development, Republic of Korea, and (iv) an Interuniversity Transfer Agreement for the support of Oyeon Kum. We specially thank Bill Ashurst, Brad Holian, Harald Posch, and the anonymous referee who suggested the material in section 8, for useful and constructive comments on many aspects of this work.

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