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# Molecular-Based Study of Fluids

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# Historical Development and Recent Applications of Molecular Dynamics Simulation

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*The development of molecular dynamics is traced from Galileo's day to present day computation. Several applications are described. These indicate the broad scope of present day molecular dynamics: location of phase equilibria, characterization of both linear and nonlinear transport problems, simulation of solid-phase plastic flow, and simulation of fluid-phase shock waves.*

**M**OLECULAR DYNAMICS IS THE STUDY of molecules in motion under the influence of intermolecular forces. The first studies of molecular motion were applied mainly to gases, because gases, in which particles move about freely, were easiest to investigate. Although it was realized even before 1900 that the same treatment could, in principle, be applied to liquids and solids, these did not become important subjects of molecular dynamics until the advent of fast computers. A complete historical review can be found in Reference 1.

As a separate field, molecular dynamics is barely 100 years old, dating from Maxwell's and Boltzmann's introduction of statistical methods to study large numbers of particles. But its origins go back to the beginning of true scientific endeavor by Galileo nearly 400 years ago. Galileo Galilei (1564–1642) was the first to experiment systematically with moving objects, finding laws for velocity and acceleration. Around the same time, Johannes Kepler (1571–1630) labored to formulate the laws of planetary motion. Isaac Newton (1642–1727) combined and generalized the discoveries of Galileo and Kepler to show that the force acting on falling objects on earth and on celestial objects was the same, that of gravity. Newton also developed calculus—the mathematical machinery needed to describe, through his laws of motion, a complete mechanical view of the universe. His precise treatment of mechanical phenomena has had an overwhelming impact and a validity unchallenged until quantum mechanics and relativity theory arrived in this century.

Eighteenth century scientists generalized and applied Newton's laws. Two Swiss colleagues, Leonhard Euler (1707–80) and Daniel Bernoulli (1700–82), fruitfully combined mathematics with mechanics. Euler conceived the principal formulas of fluid dynamics. He formulated the equations of motion for simplified macroscopic fluid models. Bernoulli developed macroscopic models for fluids and solids that included wave motion.

Near mid-eighteenth century, Euler's protégé, Joseph Lagrange (1736–1813), produced a general variational description of Newtonian mechanics which became known as Lagrangian or analytical mechanics. A more general formulation of mechanics, which was later seen to underlie quantum mechanics, was embodied in 1834 in Hamilton's "principle of least action." William Rowan Hamilton (1805–65), child prodigy in languages as well as mathematics, generalized Newton's equations into a form in which particle paths can be represented as minimal paths, and from which Lagrangian and Newtonian mechanics follow logically. Hamilton's principle grew out of an analogy with his main research in optics, which is related to modern wave mechanics.

The dynamical studies that resulted from Newton's work emphasized both celestial motion and that of tangible earthly matter. Eighteenth century experimenters formulated the gas laws to describe their observations on the relations between pressure and volume, and later temperature, of gases. Extension of the macroscopic laws of motion to the molecular level came much later, in spite of the fact that particle theories of matter go back to suggestions by Leucippus, Democritus, and Epicurus around 400 B.C. (Greek *atomos* means indivisible). But Aristotle, for whom metaphysics, not the objective world, was basic reality, rejected the atomic notion. His prestige caused the particle idea to be suppressed during long centuries of Aristotelian supremacy. By the seventeenth century, the idea hesitantly reappeared. Newton cautiously assumed a corpuscular view of matter, but avoided detailing it; his ideas of inertia, momentum and gravity did not depend on the ultimate division of matter.

The first to relate experimental gas law results to a dynamical theory involving motion of gas particles was Daniel Bernoulli. Bernoulli showed mathematically that gas pressure comes from the impact of minute gas particles against a surface. At the time, this original kinetic theory had astonishingly little effect on scientific thought. Bernoulli's theory was too advanced for his time and could not be accepted until more was learned about the nature of heat and the nature of particles themselves.

Heat was a puzzling phenomenon to early scientists. Was it a substance or was it motion? Orthodox opinion dating from the Greeks held it to be a distinct material. But Francis Bacon (1561–1626) claimed, "Heat itself, its essence and quiddity, is Motion and nothing else." In Newton's time, Robert Hooke (1635–1703) concluded that "heat is nothing but a

brisk agitation of the insensible parts of an object." But the eighteenth century, dominated by the concept of heat as a measurable quantity, rejected the vague idea of heat as motion, even after Bernoulli gave it mathematical precision in 1738 in his kinetic theory. The continuing official viewpoint into the nineteenth century regarded heat as a tangible fluid substance transferred from hot to cold objects, to which the name *caloric* was given in 1787 by Antoine Lavoisier (1743–94). Doubts were cast over the caloric theory by Benjamin Thompson, Count Rumford (1753–1814), an ingenious American turned European, whose observations on heat appearing in the process of boring cannons convinced him by 1804 that heat is vibratory particle motion. His ideas were taken further by the German physician Julius Mayer (1814–78), who in 1842 suggested the general principle of conservation and equivalence of all forms of energy. Within a year, Mayer's radical proposal was verified by careful experiments on the mechanical equivalent of heat performed by James Prescott Joule (1818–89) in his Scottish brewery laboratory.

The concept that heat and work were equivalent manifestations of energy formed the basis for the science of thermodynamics, and is stated in its first law. The principle underlying the second law appeared in the 1824 memoir of Sadi Carnot describing his work on efficiency of steam engines. But not until 1852 did William Thomson, later Lord Kelvin (1824–1907), formally proclaim the "universal tendency in nature to the dissipation of mechanical energy." Thomson's dissipation principle was given its modern focus in 1865 when Rudolf Clausius (1822–79) devised the word *entropy* for describing the irretrievable degradation of all forms of energy into heat.

The law of increasing entropy, by introducing a one-way direction to the workings of nature, was a major jolt to the mechanistic Newtonian system, which apparently could run just as well backwards as forwards. The reversibility of Newton's equations is only apparent, not real, because the equations are mathematically unstable for strongly coupled degrees of freedom. This means that a small change in initial conditions leads to catastrophic changes in subsequent particle trajectories; the numerical precision required to reverse trajectories grows exponentially with elapsed time. Any tiny fluctuation, as is always found in real systems, suffices to introduce mathematically irreversible behavior.

While macroscopic thermodynamics studied heat and energy, microscopic particle motion was clarified early in the nineteenth century through chemistry. Direct contact with then-hypothetical particles being impossible, it was left to chemists to establish atoms by examining chemical combinations of various substances. John Dalton's studies of combining ratios in compounds resulted in the law of multiple proportions. Gay-Lussac in France also investigated chemical reactions. Neither made a distinction between atoms and molecules. It was the task of Amadeo

Avogadro (1776–1856) to show, in 1811, that the ultimate *atoms* combine into divisible *molecules* (*molecule* means little masses in Latin). The discovery in 1827—not then understood—by biologist Robert Brown (1773–1858) of the continual agitated motion of particles viewed through a microscope later gave strong support to the atomic-molecular theory, by explaining Brownian motion as a result of molecular bombardment. At the end of the nineteenth century, Paul Langevin (1872–1946), in his work on molecular structure, helped link Brownian motion to kinetic theory.

The chemical concept of molecular structure joined with the thermodynamic notion of heat to advance kinetic theory. Joule went on from his heat-work measurements to calculate in 1848 the average velocity that molecules must have to produce an observed pressure by impact on a container—Bernoulli's work was being vindicated. About 10 years later, Clausius described a model of elastic spheres colliding and studied gas diffusion. Lord Kelvin, early a supporter of Carnot, Joule, and Clausius, used his prestige to establish kinetic theory. James Clerk Maxwell (1831–79), best known for electromagnetic discoveries, had an equally great influence on kinetic theory by his idea of average velocity of gas molecules within a sample, with actual velocities being distributed probabilistically.

If to Maxwell goes the credit for first applying probability to kinetic theory, the development of Maxwell's idea and its relation to thermodynamics was the achievement of Ludwig Boltzmann (1844–1906). Boltzmann stated the law of increasing entropy in terms of the tendency for molecular motion to become more random or disordered. Boltzmann attempted to justify Maxwell's hypothesis by relating statistics and entropy by means of his H-theorem. His work was the real start of statistical mechanics, which, by applying probability to molecular motion, avoids the need to follow the time development of particle trajectories.

In 1873 J. D. van der Waals (1837–1923) in Holland included in kinetic theory actual sizes of molecules and introduced intermolecular forces. His work showed that kinetic theory could explain not only properties of gases, but also the transition between gas and liquid. By the turn of the century, J. Willard Gibbs (1839–1903) had constructed a general statistical mechanical method applicable to all three states of matter. In 1916, solutions to Maxwell's transfer equations were given by Sydney Chapman (1888–1970). In the following year, David Enskog (1884–1947) similarly solved the Boltzmann equation describing the dynamical evolution of gases. This double solution made it possible to compare kinetic theory with viscous flow and heat conduction experiments and also predicted thermal diffusion, later found experimentally.

Just after the turn of the century, Max Planck (1858–1947) introduced his revolutionary quantum hypothesis, showing that energy levels (in

electric oscillators) were quantized, or limited to discrete values that are multiples of a definite quantum of energy. That natural phenomena do actually proceed by jumps and not continuously as envisioned by Newton's mechanics and its tool, calculus, was a blow even to Planck. His discontinuity hypothesis was initially viewed with suspicion. Einstein's explanation of the photoelectric effect finally helped quantum theory gain acceptance as an abstract system explaining discrepancies between Newton's laws and observed reality. Although conceptually closer to reality than classical mechanics, quantum mechanics, through the uncertainty principle, adds enormous calculational difficulties to treating real materials. Consequently, in statistical mechanics and in molecular dynamics, classical Newtonian mechanics remains a functional tool, actively used to this day.

### *Equations of Motion and Forces*

Kinetic theory, armed with statistical averaging techniques that make it feasible to treat large numbers of particles, provides the theoretical basis for the actual calculations of molecular motion undertaken by molecular dynamics. These molecular dynamics calculations consist of series of "snapshots" of particle coordinates and momenta that closely satisfy microscopic equations of motion. For many years such intricate studies involved too much calculation to permit meaningful results, but nearly 40 years ago computing technology became sufficiently advanced to be applied fruitfully to many-body systems. At about this time, progress changed from the sort of individual endeavor of previous centuries to organized team work, resulting from the changeover to computer aided scientific activity.

The early molecular dynamics calculations were carried out at the University of California's Los Alamos and Livermore laboratories, where computers became available as a fringe benefit of weapons work. Modelled on celestial mechanics, with molecules represented by mass points interacting with central forces, these calculations led to rapid advances in both equilibrium and nonequilibrium systems (2, 3). Computational teamwork tested the validity of the equilibrium statistical mechanics of Gibbs, and the kinetic theory of Boltzmann and Maxwell. The computer results showed that Boltzmann's equation does correctly describe the approach to equilibrium and that the equation of state derived from statistical Monte Carlo averaging agrees with that found by dynamical time-averaging (4, 5).

The more recent proliferation of molecular dynamics calculations to dozens of institutions makes it impossible and even undesirable to present a comprehensive review of developments. The enormous increase produced some welcome duplications and verifications of results as well as

less welcome computations of questionable value. The growth of low-cost computing has so facilitated calculation that it has become simpler to calculate than to understand the theory underlying the numbers. Even a very slow machine can readily produce too much output for a competent investigator to explain. Thus the most relevant advances in software are those that speed assimilation of computed information. Particularly valuable are stereoscopic plotting routines, contour plotters, and automatic movie-making devices. These features greatly reduce the amount of the researcher's time necessary for interpretation.

Definite accomplishments of recent calculations include a complete description of the equilibrium fluid and solid phases for particles interacting with the argonlike Lennard-Jones interparticle potential (inverse 6th power attraction and inverse 12th power repulsion) (6-8), the development of increasingly accurate liquid-phase perturbation theories (9, 10), based on hard-sphere, computer generated properties that closely reproduce these equilibrium properties, and new methods for measuring thermodynamic and transport properties as functions of volume and energy for a wide range of force laws.

The simplest force-law models of Boltzmann and van der Waals viewed particles as hard spheres or billiard balls with mutual attractions added to explain gas-liquid coexistence. Empirical "force laws" describe the mutual interaction of molecules as a function of their relative orientation and separation. Solid-phase calculations emphasize force-law derivatives and were instrumental in developing the many analytic "potentials" (integrated forces) used in the last 30 years.

Two distinct kinds of extensions have been made from the early mass-point calculations (11-14). First, bigger polyatomic molecules have been treated, although such calculations take one or two orders of magnitude longer than atomic ones. Second, the microscopic effects of macroscopic thermodynamic heat and work have been included by incorporating temperature and strain-rate constraints in the equations of motion (15, 16).

The most straightforward approach to polyatomic problems, treating each molecule as an aggregate of mass points interacting with its neighbors through central forces, is not physically realistic. Intramolecular angle-dependent and multipolar forces are required to study even relatively simple dynamical problems. Evans simulated the dynamics of benzene molecule collisions (17), while Helfand and Weber (18, 19) studied the torsional motions of long aliphatic carbon chains (*see* Figures 1 and 2). The successful treatment of polyatomic molecules such as benzene as rigid bodies by Evans resurrected interest in Hamilton's quaternions, angular analogs of vectors which are dynamically better behaved than Euler's angles.

Following the motion of large molecules made up of dozens of atoms

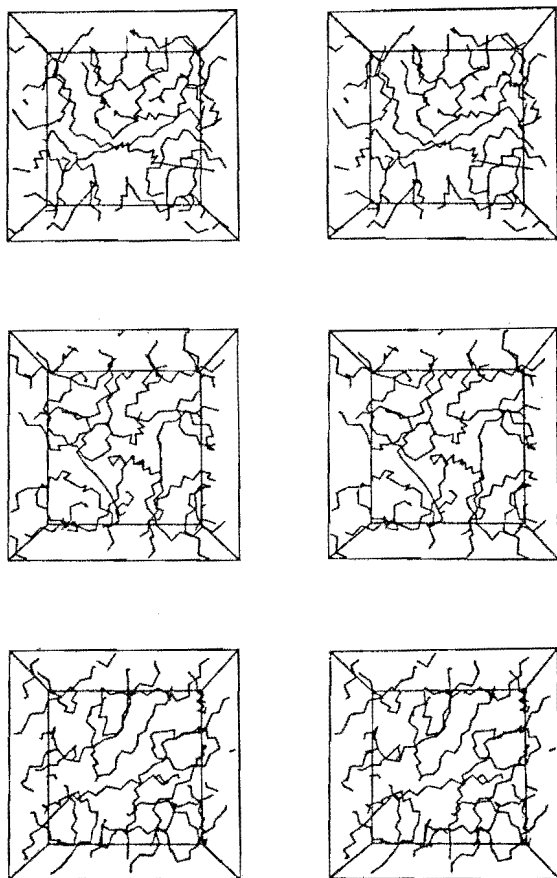


Figure 1. Stereo views of a 200-atom aliphatic carbon chain. (Reproduced with permission from Ref. 18. Copyright 1980, American Institute of Physics.)

taxes even large computers and has led to the use of approximate statistical models, based on Langevin's ideas, for simulating the interaction of such molecules with the surrounding medium. Langevin originally used statistical interactions to explain Brown's observations on moving pollen grains. The postulated and largely unknown random forces can be assigned in many ways—producing either the velocities or the accelerations characteristic of a certain temperature, for instance. Because the choice influences final nonequilibrium results, complete calculations are essential to validate these ad hoc models.

Validation is becoming more difficult. Polyatomic simulations are today moving rapidly toward increased realism (*see* Figure 3) at the cost of complexity and kinematic indeterminacy. The latter loss, inherent in



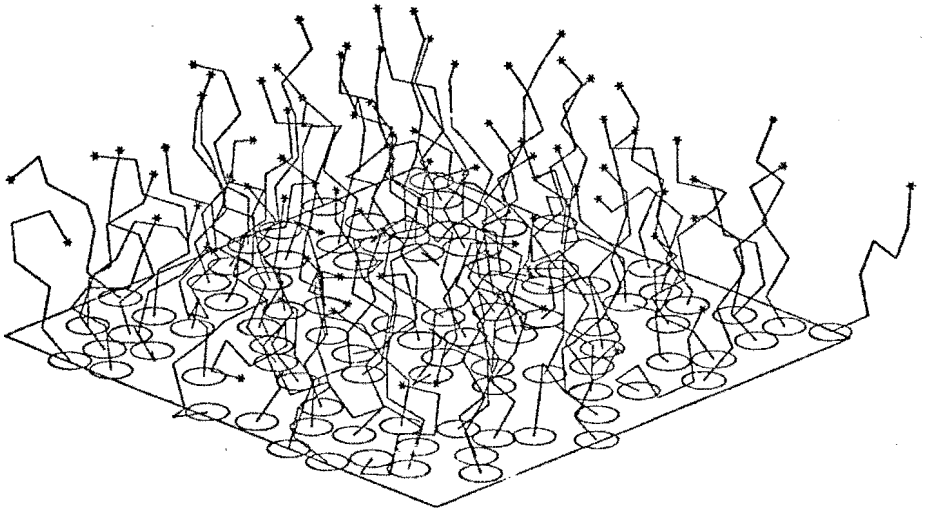


Figure 2. Conformation of a lipid monolayer. (Reproduced with permission from Ref. 14. Copyright 1980, Nature.)

random forces, complicates numerical verification because reversibility of the equations of motion and conservation of energy and momentum can no longer be used to test solutions.

The complexity introduced into polyatomic deterministic simulation by the wide range of time scales between slow conformational degrees of freedom and fast bond oscillations may be reduced if a new method suggested by Pechukas proves feasible. Because details of the bond oscillations are ordinarily of little interest, Pechukas has treated these as sources and sinks of energy to be added to a rigid-bond Hamiltonian. This added energy varies with molecular conformation to conserve the action of the oscillating modes. Including the extra energy leads to exact equations of motion for the conformational degrees of freedom in the adiabatic (high-frequency) limit. The obstacle to practical use of this method has so far been the difficulty of separating the conformational and vibrational degrees of freedom.

On a microscopic scale, molecular dynamics measures temperature by averaging kinetic energy. Gradual temperature changes can be imposed by continuously scaling the momenta of the particles during dynamical calculations, thereby adding or subtracting heat energy from the simulation. Gradual adiabatic changes can similarly vary the energy by performing pressure-volume work in a way consistent with the first law of thermodynamics. Both momentum scaling and adiabatic coordinate scaling have been successfully incorporated in microscopic equations of motion.

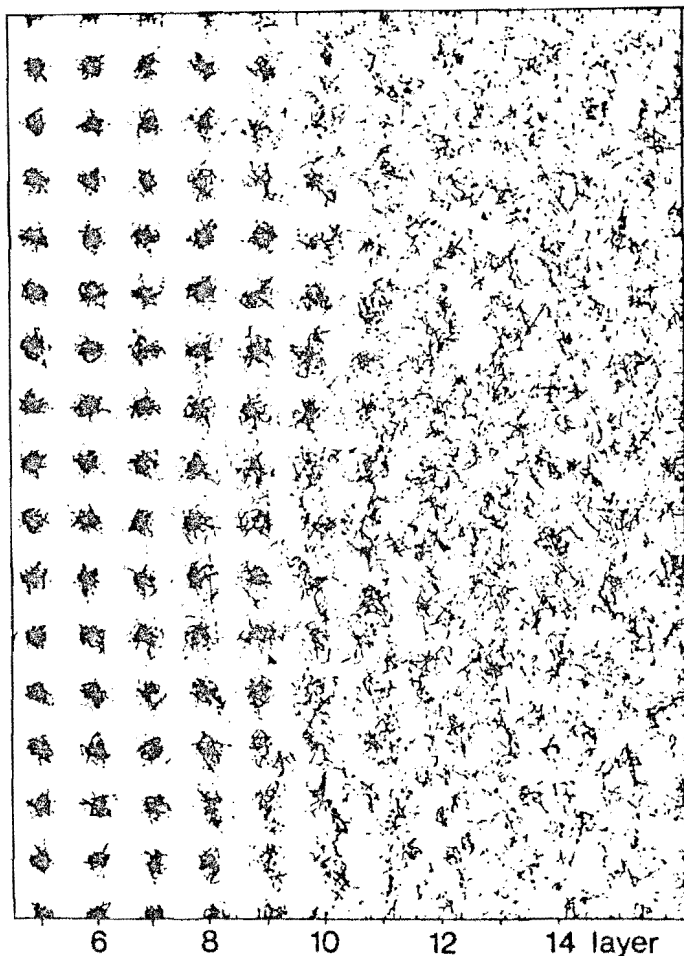


Figure 3. Time exposure of a solid-fluid interface. (Reproduced with permission from Ref. 22. Copyright 1980, American Institute of Physics.)

### *Application to Phase Equilibrium*

The rough corresponding states similarity among phase diagrams of widely varying substances suggests that even very simple interparticle-force models can explain the qualitative properties of real matter. The classical calculations of Alder, Wainwright, and Wood, based on hard-sphere, square-well, and Lennard-Jones force laws, justified this expectation by reproducing, qualitatively, the solid-fluid melting line and gas-liquid-solid triple-point equilibria found in real systems (20).

A few phase diagrams that include quantum corrections have been calculated. Hansen's plasma calculations in France (21) and the ongoing

calculations of Ceperley and Alder at Livermore on the absolute zero phase diagrams of boson and fermion systems represent the present limit of numerical quantum statistical mechanics. These equilibrium quantum calculations are much more time consuming and intricate than the corresponding classical ones. They can be carried out only at low temperature, where the ground state is important, or at temperatures high enough for perturbation theory to be applied to the classical theory. Rigorous quantum calculations cannot yet deal with the complications involved in intermediate-temperature or time-dependent systems.

Some early Lennard-Jones and square-well calculations encountered two-phase liquid-vapor states. These states were qualitatively interesting to see, but were quantitatively difficult to analyze, simply because interfacial boundaries are relatively thick on an atomic scale. Cape, Ladd, and Woodcock (22, 23) have used simulations of equilibrating phases, both at the triple point and along the melting line, as primary means of locating equilibrium pressures and temperatures and determining interfacial properties. Such calculations require many particles (as many as 7680 were used) and care in choosing initial conditions. Now, approximate equilibria are first obtained using smaller systems. Several similar small systems are then grouped to make a large compound system for further examination. The "time exposure" of a solid-fluid interface shown in Figure 3 indicates the detail obtainable in surface morphology.

The coexisting-phase properties obtained by these direct equilibrations are consistent with earlier triple-point thermodynamic predictions based on single-phase free-energy simulations with far fewer particles. This is only one of many examples in which self-consistency between two or more approaches has confirmed the accuracy of computer generated data in regions where rigorous theory gives little a priori guidance. Nonequilibrium effects are important to the direct simulation of coexisting phases because the equilibration of large phases is controlled by heat diffusion. The computational difficulty due to heat diffusion can be sidestepped by carrying out the molecular dynamics isothermally (15, 24). If Newton's equation of motion,  $\dot{p} = F$ , has added to the right side a momentum dependent force  $-\zeta p$ , then the constant-temperature constraint  $d/dt \sum p^2 = 0$  can be identically satisfied by choosing  $\zeta = \Sigma F \cdot p / \Sigma p \cdot p$ . The resulting trajectories conserve kinetic energy and provide an example of what we call *nonequilibrium* molecular dynamics, in which the equations of motion are modified to satisfy desirable constraints, at the expense of energy conservation.

### *Application to Fluid Transport*

The conceptually simplest nonequilibrium situations involve linear flows of mass, momentum, and energy proportional to the corresponding

gradients of chemical potential, velocity, and temperature. These simple prototype flows form a convenient bridge between the well understood statistical mechanics, which can describe linear transport by dynamical perturbation theory, and the largely undeveloped theory of nonequilibrium nonlinear flows.

Viscosity, principally shear viscosity (the response of stress to changes in shape), dominates nonequilibrium flows, determining whether these are turbulent or laminar. Three different molecular dynamics methods have been used to compute the coefficient of shear viscosity. To demonstrate the simplest type of shear deformation, suppose that the fluid's  $x$  velocity component is proportional to the  $y$  coordinate,  $\dot{\epsilon} = du_x/dy$ . Such a deformation can be described using Hamiltonian mechanics. The so-called "Doll's Tensor" Hamiltonian,

$$H = H_{\text{eq}} + \dot{\epsilon} \sum y p_x$$

was inferred from the corresponding equations of motion (25),

$$\dot{q} = (p/m) + q \cdot \nabla u \quad \text{and} \quad \dot{p} = F - \nabla u \cdot p$$

which reproduced exactly the desired macroscopic flow field and also led to the macroscopic energy conservation relation between  $P_{xy}$  and the strain rate  $\dot{\epsilon}$ . The shear viscosity  $\eta$  can also be obtained by applying Green-Kubo linear response theory to the nonequilibrium Hamiltonian in the limit of vanishing strain rate  $\dot{\epsilon}$ , with the result that  $P_{xy} = -\eta\dot{\epsilon}$  where  $\eta$  is the shear viscosity

$$P_{xy} = -\dot{\epsilon}(V/kT) \int_0^\infty \langle P_{xy}(0)P_{xy}(t) \rangle_{\text{eq}} dt$$

Thus, the time-averaged decay of equilibrium pressure fluctuations can be used to give estimates of transport coefficients (26). Holian has recently shown (27) that for finite systems the two viscosities just described can differ. Computer simulations suggest that the number dependence is reduced by using the Doll's Tensor approach.

The linear-response approach has been followed more literally and less formally by Jacucci and coworkers (28) who actually applied a finite but still very small perturbation. Then the difference between the two slightly different dynamical many-body trajectories—one perturbed and the other unperturbed—was followed in time, and the resulting stress differences used to estimate the viscosity coefficient. The nonlinear response to the same form of perturbation has been studied too, through the steady state that develops with a large and continual isothermal rate of shear (29).

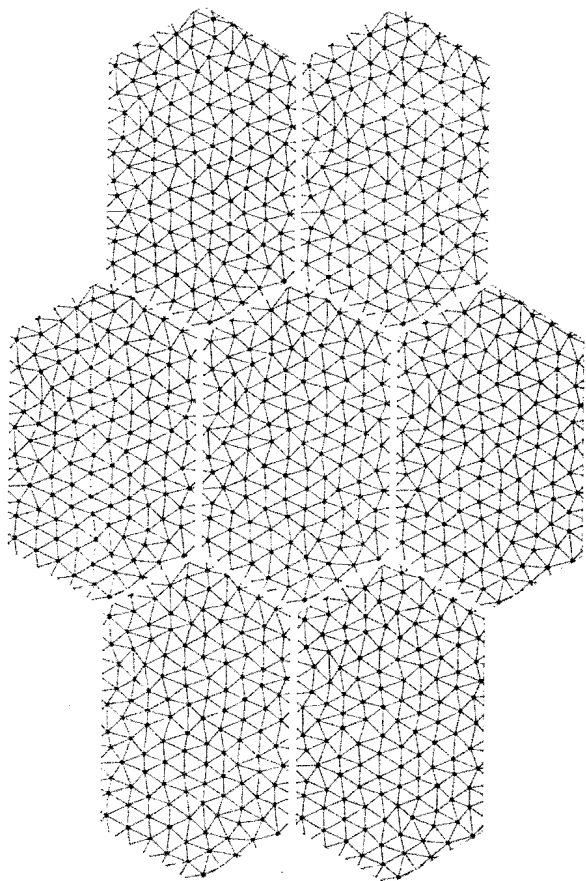
These three methods for determining viscosity agree fairly well with each other and with real viscosity measurements. They agree also in predicting a shear-thinning decrease in viscosity with increasing frequency or strain rate (30). The viscosity decrease is not well understood, exceeding, by orders of magnitude, predictions based on the corresponding mode-uncoupling theories.

Analogous calculations for bulk viscosity (the irreversible response of stress to changes in volume) require the periodic adiabatic dilation and compression of space simultaneously with the molecular dynamics calculations. These calculations reveal a variation of viscosity with dilation frequency stronger than theoretical predictions and evidently quite unrelated to the experimental frequency dependence (31, 32)—which apparently diverges as  $\omega^{-5/2}$  at low frequency. The computer results have pointed out the need to revise the 1926 Chapman–Enskog bulk viscosity theory, which overpredicts bulk viscosity by nearly an order of magnitude under some conditions and which also fails to explain either of the low-frequency bulk viscosities observed in laboratory or computer experiments. Ultrasonic data suggest a very strong frequency dependence of the moderate-density bulk viscosity, but Hickman and Hoover, applying nonequilibrium molecular dynamics to that problem, found considerably smaller values for frequencies large enough and system sizes small enough for computer simulation.

Most computer flow simulations are necessarily nonlinear, so that the pressure-tensor perturbations caused by the deformations can be distinguished from background thermal fluctuations. The nonlinearity has interesting consequences. A system undergoing adiabatic compression, for instance, deviates in its pressure by a bulk viscous term proportional to the strain rate. The virial theorem has been used (16) to show that along with this pressure shift there is a corresponding temperature shift, so that the strain-rate-caused deviations of  $P(T, V)$  and  $P(E, V)$  from the equilibrium pressure are not the same.

Nonlinear effects are sometimes controversial: The coupling of heat flow with rotation is an example. According to Boltzmann's low-density kinetic theory, Coriolis's accelerations in rotating systems can prevent heat flow from paralleling the temperature gradient. On the other hand, certain formal approaches to macroscopic continuum mechanics rule out such violations of Fourier's law (33). The direction of the heat flow was studied using nonequilibrium molecular dynamics (34). A dense, two-dimensional fluid, constrained to rotate at constant angular velocity in the presence of a temperature gradient, developed a heat flux in good agreement with the predictions of Boltzmann's kinetic theory.

The same adiabatic perturbation to the Hamiltonian used to shear fluids is being used to study dislocation motion in solids (*see* Figure 4). Imperfect solids are plastically strained at relatively high amplitudes and



*Figure 4. Periodic plastic flow, an application of adiabatic nonequilibrium molecular dynamics. (Reproduced with permission from Ref. 35. Copyright 1980, Metallurgical Society of the American Institute of Mechanical Engineers.)*

gigahertz frequencies (35). By including the constant-temperature restriction, these solid-phase studies conform to fluid studies, showing an increase of shear stress with density and strain rate, and a decrease with temperature and system size (30). Results of such calculations can be compared with corresponding continuum mechanics calculations and used in macroscopic plasticity and fracture simulations. In these material failure simulations, dislocations act as point particles obeying equations of motion deduced from atomistic simulations. This work will eventually lead to improved constitutive descriptions of plastic flow in solids. The Doll's Tensor ( $\Sigma qp$ ) Hamiltonian has been applied to crystal structure

stability studies too, by treating the pressure tensor as the independent variable, which governs the time-varying strain-rate tensor (36).

Today there is a need for critical evaluation of different possible definitions of nonequilibrium nonlinear coefficients. Work now in progress, both on the theory of nonlinear flows and on their simulation, will lead to major advances in understanding rheological problems.

### *Application to Fluid Shock Wave Structure*

Slow heating and deformation could be described by equilibrium molecular dynamics, but in a case involving extremely rapid heating and deformation, such as a shock or detonation wave (37), when large changes occur in the time of only one atomic vibration, equilibrium simulations are inappropriate. Macroscopic heating usually occurs by conduction or convection from the boundary, whereas microscopic systems can easily be "heated" homogeneously throughout. Likewise, the homogeneous microscopic deformations associated with the Doll's Tensor Hamiltonian  $H = H_{\text{eq}} + \Sigma qp : \nabla u$  are more naturally replaced by shock deformation on a macroscopic scale.

Fast shock wave compression can be simulated by inhomogeneously shrinking one space dimension in a microscopic molecular dynamics simulation (see Figure 5). Laboratory shockwave studies have been undertaken in liquids, solids, and gases for years. These experiments, plus additional recent work on the structure of gas-phase shockwaves, have been particularly valuable in obtaining equation of state information under extreme conditions at pressures up to tens of megabars. The structure of weak—and therefore broad—shockwaves in solids has also been studied experimentally and used to refine constitutive flow models. Through computer simulations, fluid shock waves are fairly well understood, and some progress has been made in simulating the much more complex solid phase shock waves.

The computer shock wave, in which cold material is suddenly compressed adiabatically and in the absence of nearby boundaries to high pressure, is an ideal nonequilibrium problem because the walls that complicate both simulation and analysis are absent. Theoretical treatment of even the low-density Boltzmann limit is incomplete, so that computer simulations of dense fluid shock waves very far from equilibrium are challenging tests for macroscopic theories.

A 4800-particle molecular dynamics simulation was used to generate shock wave profiles corresponding to shock compression of liquid argon to nearly twice its normal density (37). The resulting stress and temperature profiles, shown in Figure 6, agreed surprisingly well with Navier-Stokes continuum theory, a linear theory in which the transport coefficients are assumed to be independent of the velocity or temperature

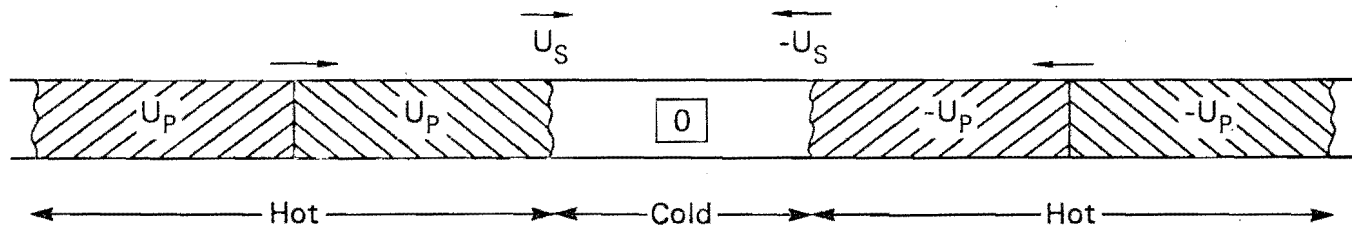


Figure 5. Shrinking boundaries moving with the piston speed  $u_p$  generate shock waves moving with speed  $u_s$ . (Reproduced with permission from Ref. 37. Copyright 1980, American Institute of Physics.)



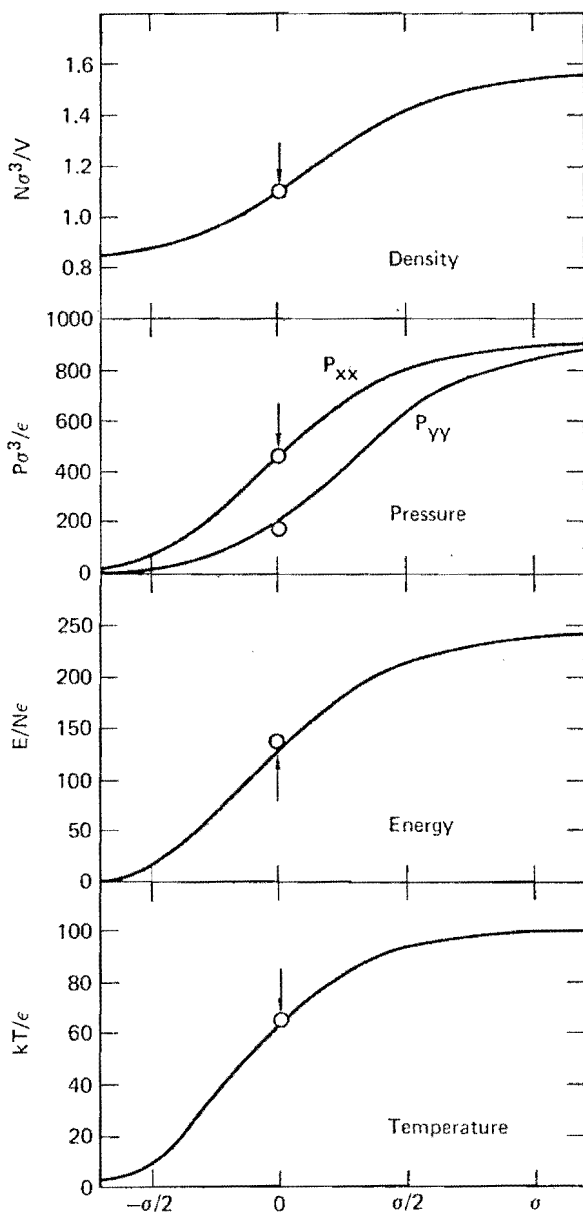


Figure 6. Profile of a strong, dense-fluid shock wave. For liquid argon, such a shock wave heats the fluid from the triple point to 1 eV in one atomic vibration time. For argon, the distance scale shown covers about 6 Å. The points were generated with nonequilibrium molecular dynamics. The smooth curves are solutions of the Navier-Stokes equations. (Reproduced with permission from Ref. 37. Copyright 1980, American Institute of Physics.)

gradients. This good agreement suggests that shockwave experiments could be used to define slowly varying nonlinear transport coefficients.

By appending chemical reactions to simulations including viscosity and conduction, the related problem of detonation wave structure can be studied. It is difficult for molecular dynamics to deliver the realism required in applications, because most real detonations are dominated by the effects of impurities. Nevertheless, models of simple liquid-phase detonations should be useful for exploring the region where chemistry is coupled with thermal and viscous effects. Except in the cases of rare-gas excitation reactions, simulations including chemistry require the development of potential surfaces for polyatomic molecules.

The natural high-pressure periodic boundary conditions have seldom been used in potential-surface calculations, but there is presently a tremendous effort devoted to representing zero-pressure polyatomic potential surfaces and incorporating these surfaces into molecular calculations. The success of these efforts should lead to an understanding of polyatomic systems on a par with today's quantitative understanding of simple fluids and solids.

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