Nonequilibrium Statistical Mechanics
The Facts and Fundamentals*

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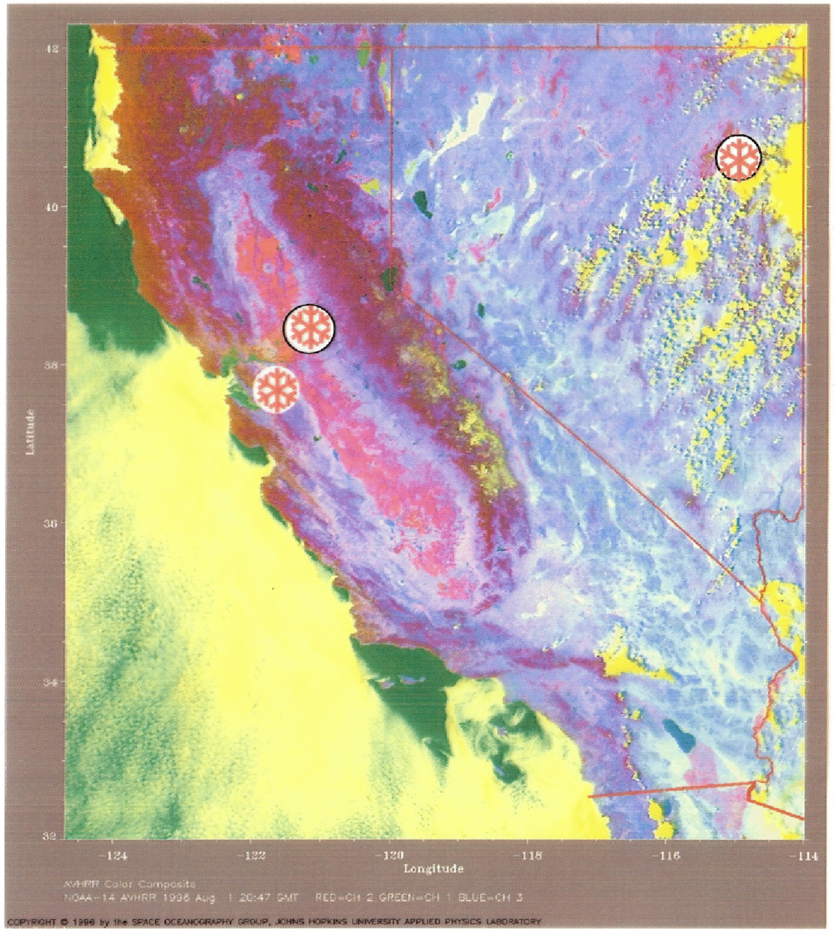
1. Physical Basis and Assumptions .
2. Numerical and Algorithmic Methods .
3. Goals of the Work .
4. Examples → Conclusions .
5. Remaining Problems .

* For Billy Todd @ Swinburne University

Overview of California and Nevada



Ruby Valley Neighbors

Local Ruby Valley Industry

MICRO-BREWED IN NEVADA'S HIGH COUNTRY

RUBY MOUNTAIN

BREWING COMPANY

VIENNA STYLE

LAGER

Nonequilibrium Statistical Mechanics
the Facts and Fundamental

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Centre for Molecular Simulation
Swinburne University of Technology

1. Physical Basis and Assumptions

Physical Basis and Assumptions

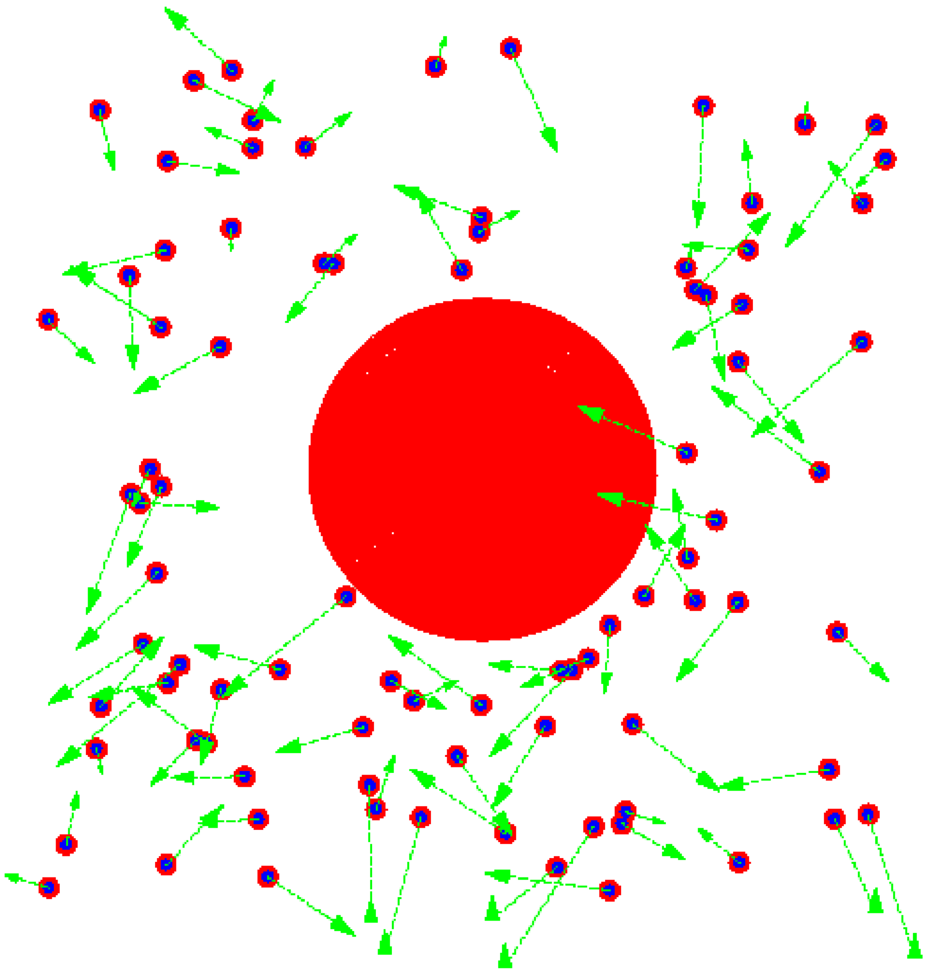
1. **Kinetic Theory → Temperature**
2. **Particle Dynamics → Pressure**
3. **Runge-Kutta → Solutions**
4. $F_A + F_B + F_C + F_D \rightarrow$ **Nonequilibrium States**

Some *Nonequilibrium* state properties :

$$\{ \nabla\rho, \nabla v, \nabla e, \nabla T, \nabla \bullet P, \nabla \bullet Q \} .$$

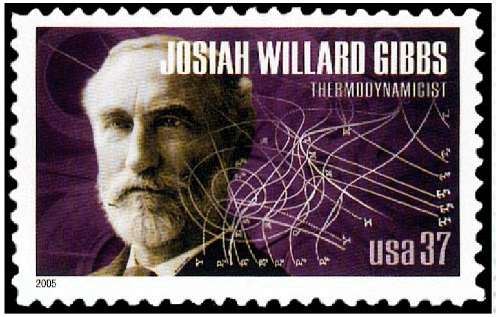
Analysis from Kinetic Theory

Ideal Gas Thermometer



Temperature is just the *comoving* Kinetic Energy .

Ideal-Gas Temperature from Kinetic Theory



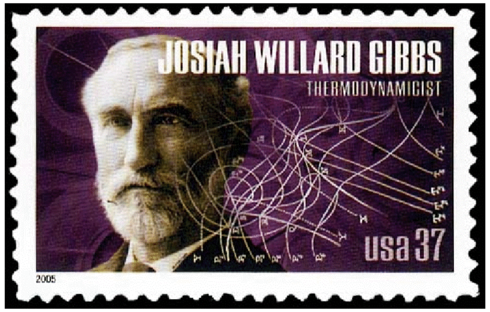
$$dv/dt \;\alpha\; -\Gamma v$$

$$dK/dt \;\alpha\; +\Gamma[\,(3kT/2) - K(v)\,]$$

Temperature is just the *comoving* kinetic energy .

Pressure *is* Momentum Flux

Gibbs' Statistical Mechanics, and Newton's Dynamics, give the *same* virial expression .

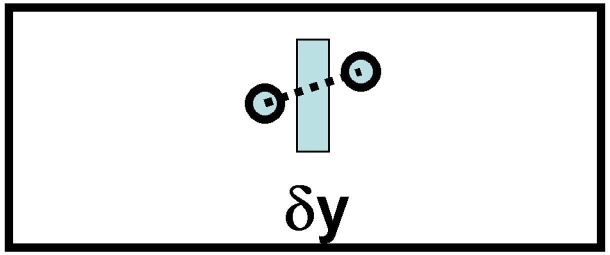


$$e^{-A(V,T)/kT} \equiv \Sigma e^{-H/kT} \text{ and } P = -(\partial A / \partial V)_T$$

$$\dot{p} = m\ddot{r} = F \Rightarrow PV = \Sigma_i (rF)_i + \Sigma(pp/m)_i$$

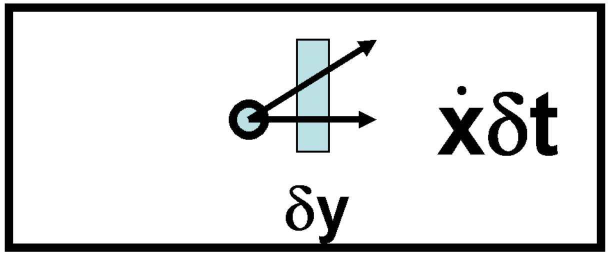
Pressure is Momentum Flux

$$P_{xx}V = < \Sigma_{ij}(x^2F/r)_{ij} + \Sigma_i(m\dot{x}\dot{x})_i >$$



Flux in x direction intersecting the element δy from particle pairs:

$$P_{\phi}\delta y = \frac{x_{ij}\delta y}{L_x L_y} F_{ij}$$



Probability of a particle with x-velocity component intersecting the element δy during time δt:

$$P_K\delta t\delta y = \frac{\dot{x}\delta t\delta y}{L_x L_y} mv$$

Molecular Dynamics Algorithms

Equations of Motion are either first-order or second-order ordinary differential equations based on the ideas of Newton, Lagrange, and Hamilton . Key concepts are conservation and constraints .

$\{\dot{q},\dot{p}\}$ or $\{\ddot{q}\}$

$\leftarrow F_C = -\varsigma p \rightarrow$

$$m\ddot{r} = m\dot{v} = F_A + F_B + F_C + F_D$$

Rogues' Gallery of Thermostaters

2. Molecular Dynamics Algorithms

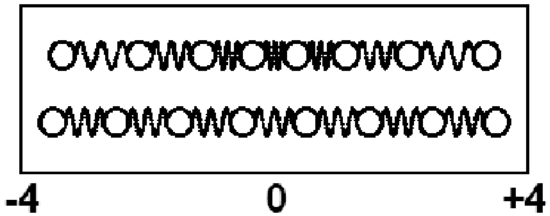
The Fourth-Order Runge-Kutta is the Simplest and most flexible algorithm .

Nonequilibrium **Flows can be induced with Boundary, Constraint, or Driving Forces .**

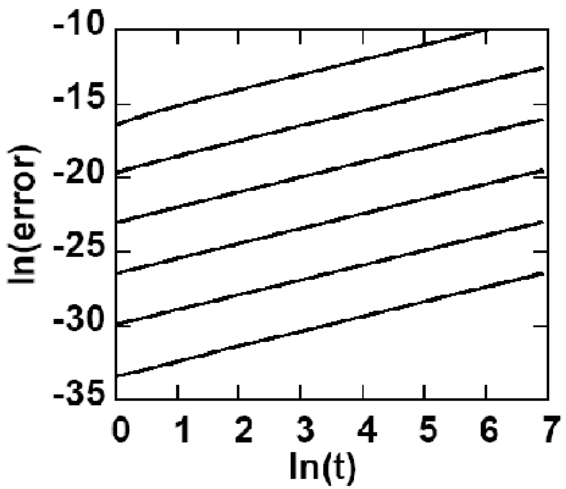
$$m\ddot{r} = m\dot{v} = F_A + F_B + F_C + F_D$$

[Thermostats, Barostats, Strain Rates]

Runge-Kutta Errors are *Small*



Eight-particle Harmonic Chain
[it has an analytic solution .]



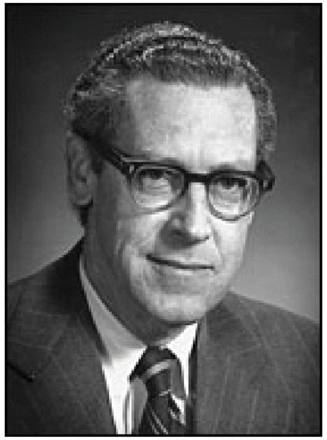
$$m\ddot{x}_i = \kappa[x_{i+1} - x_i - d] + \kappa[x_{i-1} - x_i + d]$$

$$\Rightarrow \ddot{x}_i = x_{i+1} - 2x_i + x_{i-1} \Rightarrow \omega = 2\sin(k/2)$$

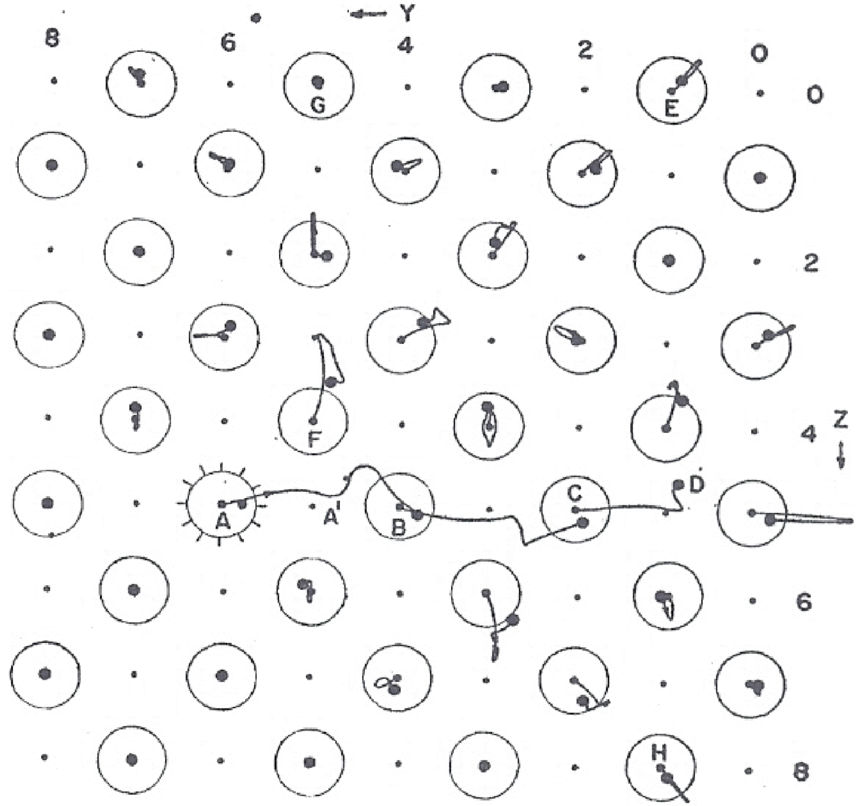
Errors in the Total Energy are shown for
Δt = 0.01, 0.02, 0.04, 0.08, 0.16, 0.32 .

2. Molecular Dynamics Simulations

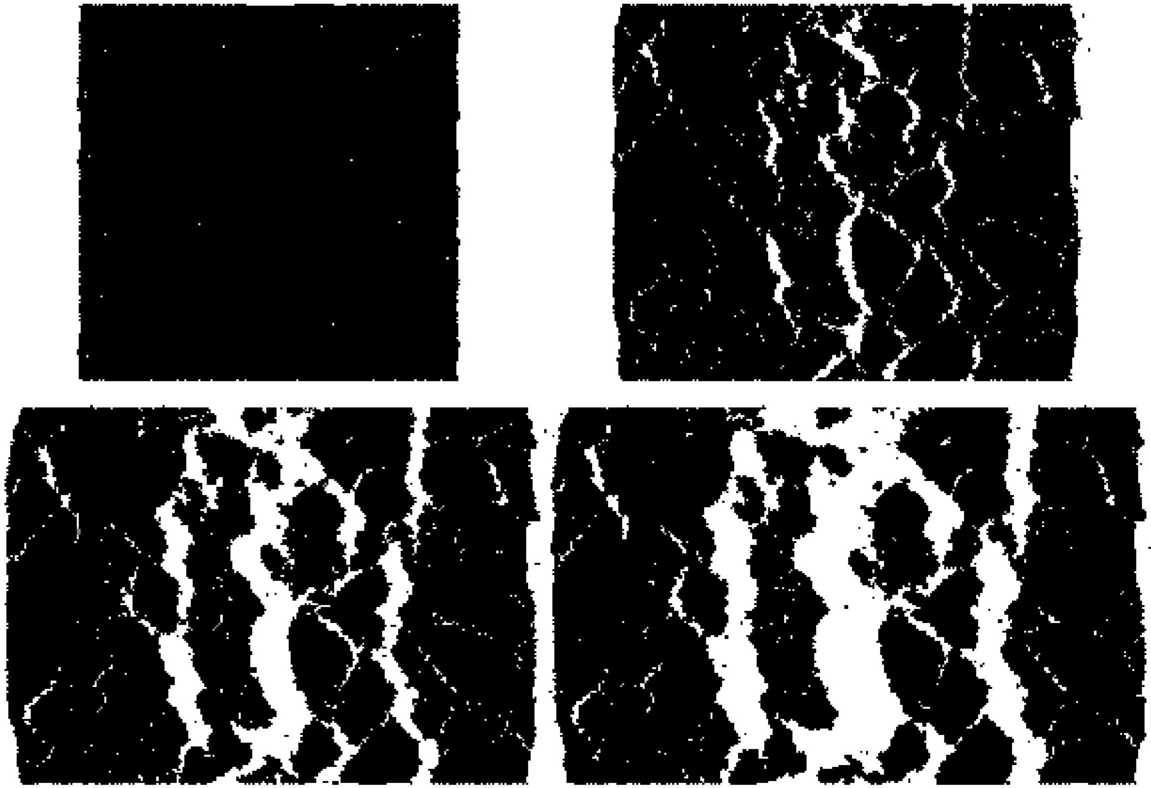
Nonequilibrium Flows can be induced By using Special Initial Conditions .



Simulating Radiation Damage to Copper With ~500 Atoms .



Typical Work Station Simulation with N = 10,000
Uniaxial Expansion after 10% Compression



Molecular Dynamics Fracture

$$\phi(r) = (2 - r^2)^8 - 2(2 - r^2)^4$$

3. Goals of the Work

The Past :

- Gibbs' and Boltzmann's Statistical Mechanics
- Green and Kubo's 1950s Transport Theory

The Present :

- The Second Law of Thermodynamics
- Eulerian and Lagrangian Continuum Mechanics
- Flow, Fracture, and Failure

The Future :

- Quantum Dynamics

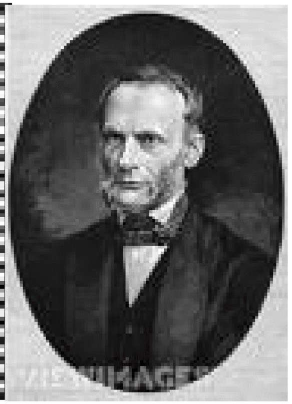
3. Fourier, Newton, and Fick

$$\mathbf{Q} = -\kappa \nabla \mathbf{T}$$

$$\mathbf{P} = [\mathbf{P}_{eq} - \lambda \nabla \bullet \mathbf{v}]\mathbf{I} - \eta[\nabla \mathbf{v} + \nabla \mathbf{v}^{t}]$$

$$\mathbf{J} = -\mathbf{D} \nabla \rho$$

3. Second Law of Thermodynamics



vs

Boltzmann: Entropy Increases (Dilute Gases) .
Kelvin: Work to Heat is ok. *Not* the reverse !
Clausius: Entropy Increases !
Loschmidt: But the Equations are Reversible !
Poincaré: But the Initial Conditions Recur !

3. Eulerian and Lagrangian Continuum Mechanics

Needs: Initial Conditions , Boundary Conditions, Constitutive Equations, *and* an Algorithm .

$$\dot{\rho} = -\rho \nabla \bullet v$$

$$\rho \dot{v} = -\nabla \bullet P \equiv \nabla \bullet \sigma$$

$$\rho \dot{e} = -\nabla v : P - \nabla \bullet Q$$

4. Examples → Conclusions

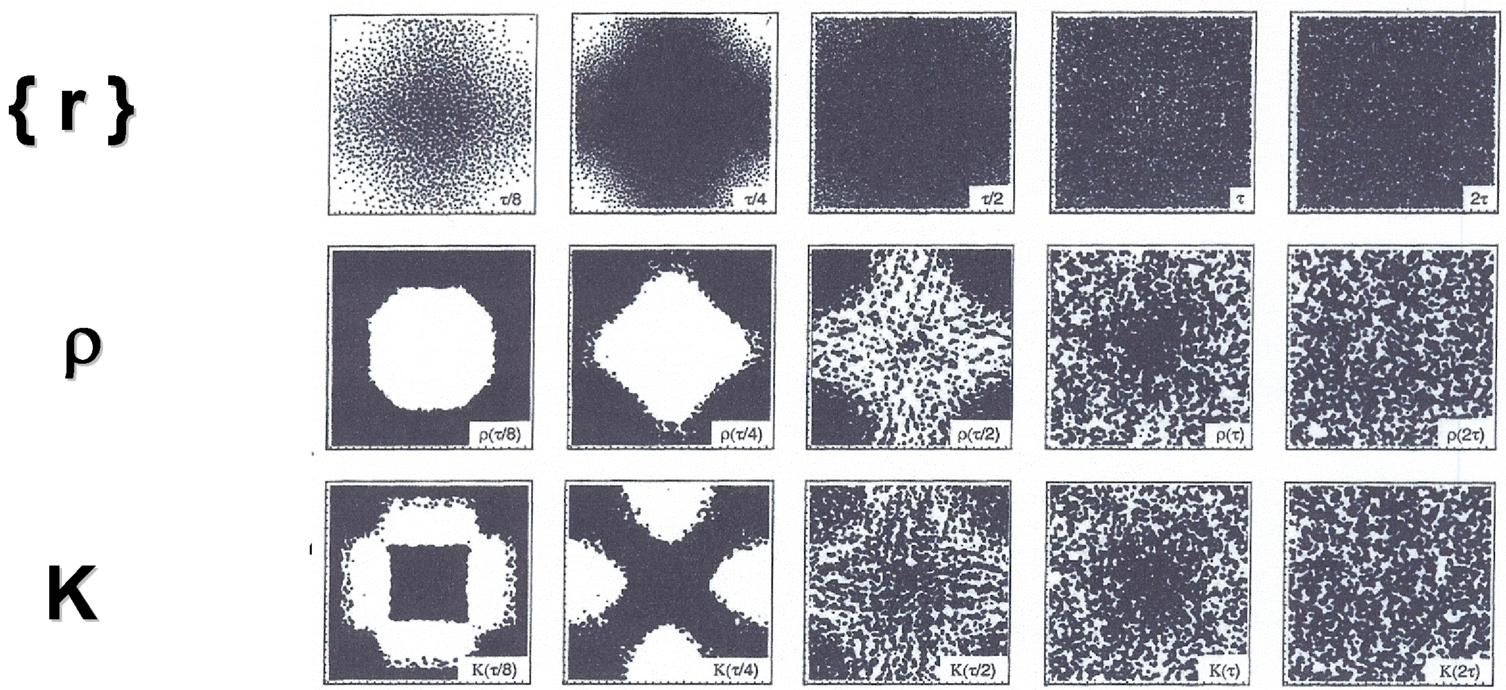
Free Expansion
→ Entropy from Fluctuations .

Shockwave Structure and Viscosity
→ Scale, Nonlinearity, Even a sign error !

ϕ^4 Model for Heat Conductivity
→ Thermostats, Fractals, Dimensionality Loss .

SPAM [Smooth Particle Applied Mechanics]
→ Continuum Mechanics with Particles !

Free Expansion of 16,384 Particles

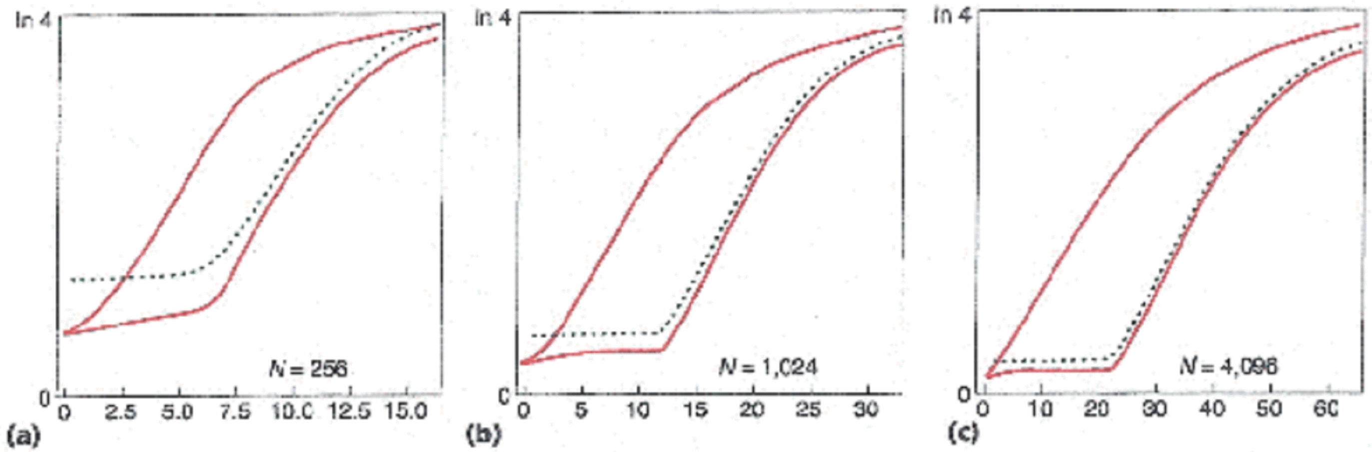


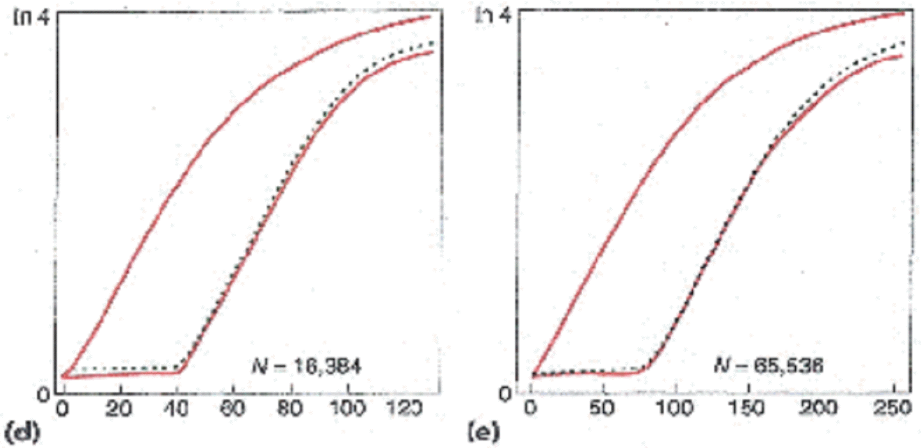
The Gibbs' Paradox Entropy ,

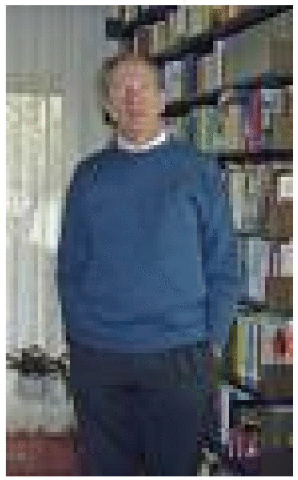
$\Delta S = Nk\ln 4$,

can be traced to fluctuations .

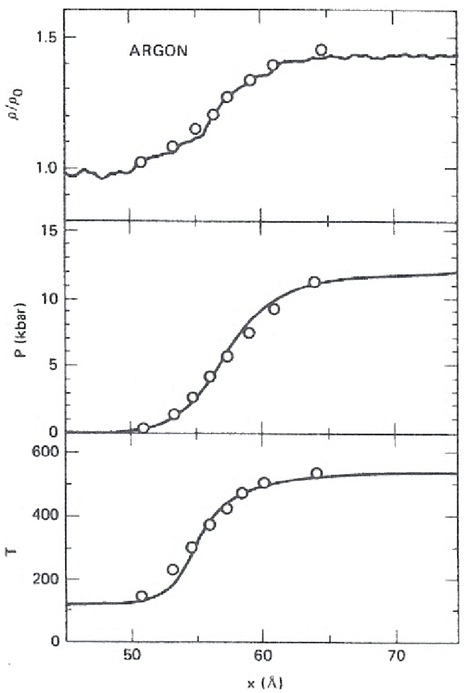
Comoving and Lab Frame Entropies



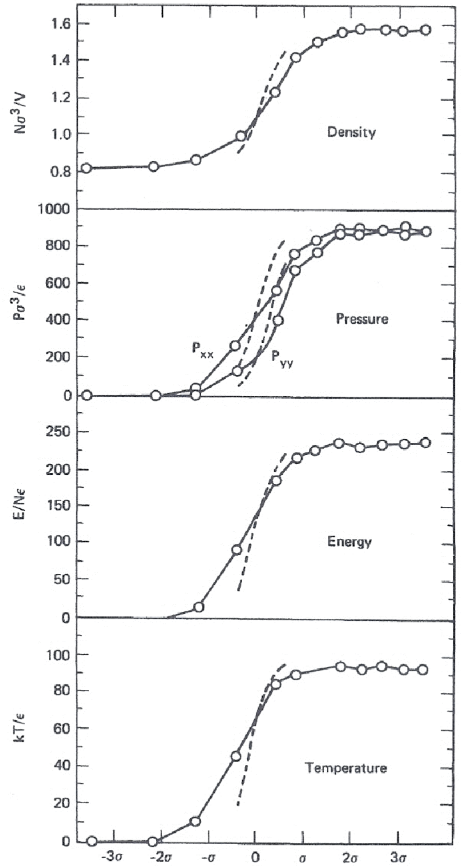




Navier-Stokes *vs* Molecular Dynamics



Navier-Stokes Shockwidths are *too Narrow* for Strong Shocks (Linear) transport Coefficients are *too Small* ! →



Weak Shocks are the same .

50% Compression with a Strong Shockwave

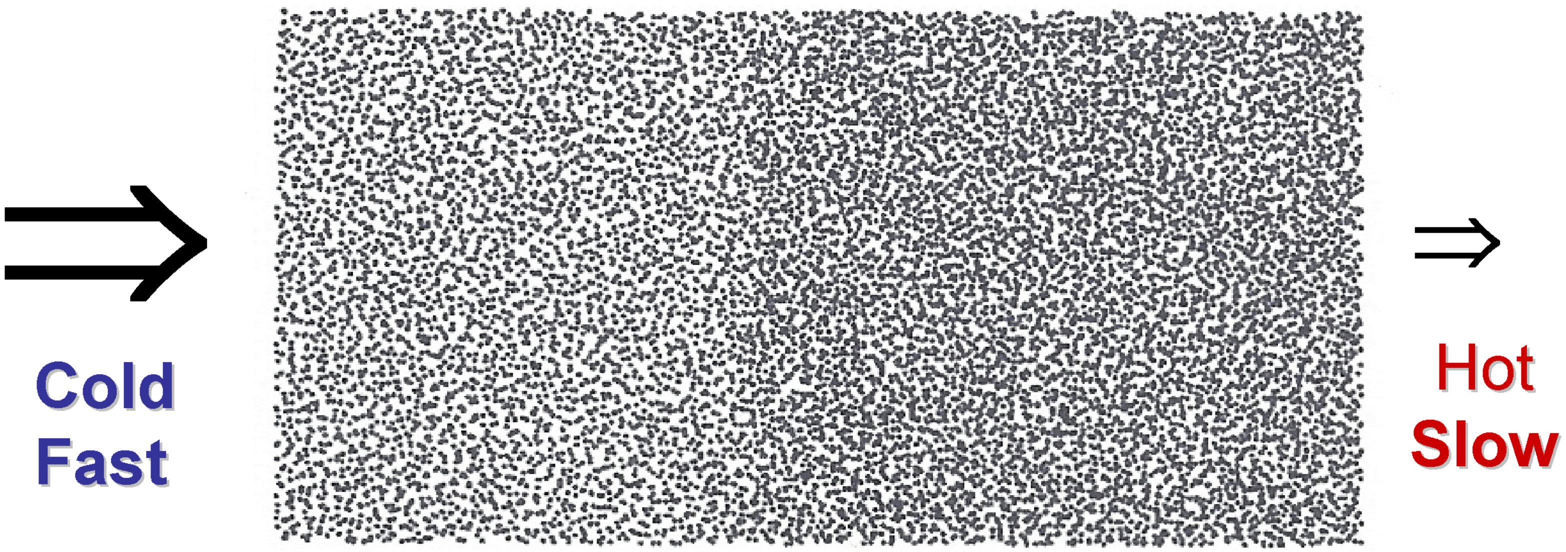
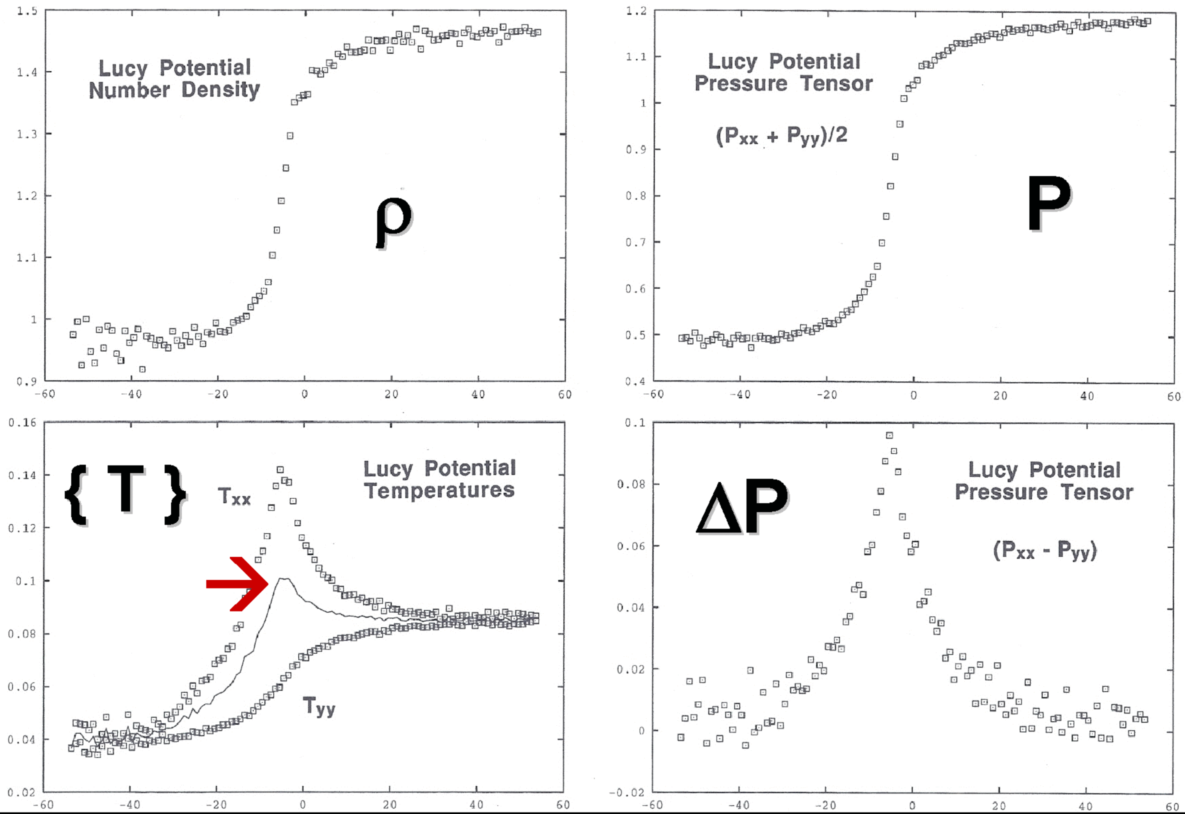


FIG. 1. Snapshot of the 12 960-particle shock wave simulation

This shockwave has quite an interesting temperature profile !

12,960-Particle Shock Profiles

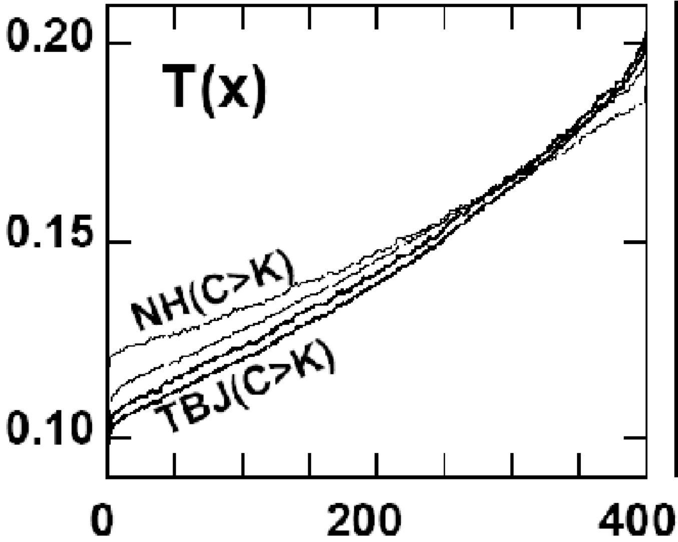


Flagrant Violation of Fourier's Law !

Conductivity of a ϕ^4 System

Travis/Braga/Jepps $kT_{LL} \equiv \langle (\nabla_q H)^2 \rangle / \langle (\nabla_q^2 H) \rangle$

Kinetic Theory $kT_{IG} \equiv \langle (\nabla_p H)^2 \rangle / \langle (\nabla_p^2 H) \rangle$

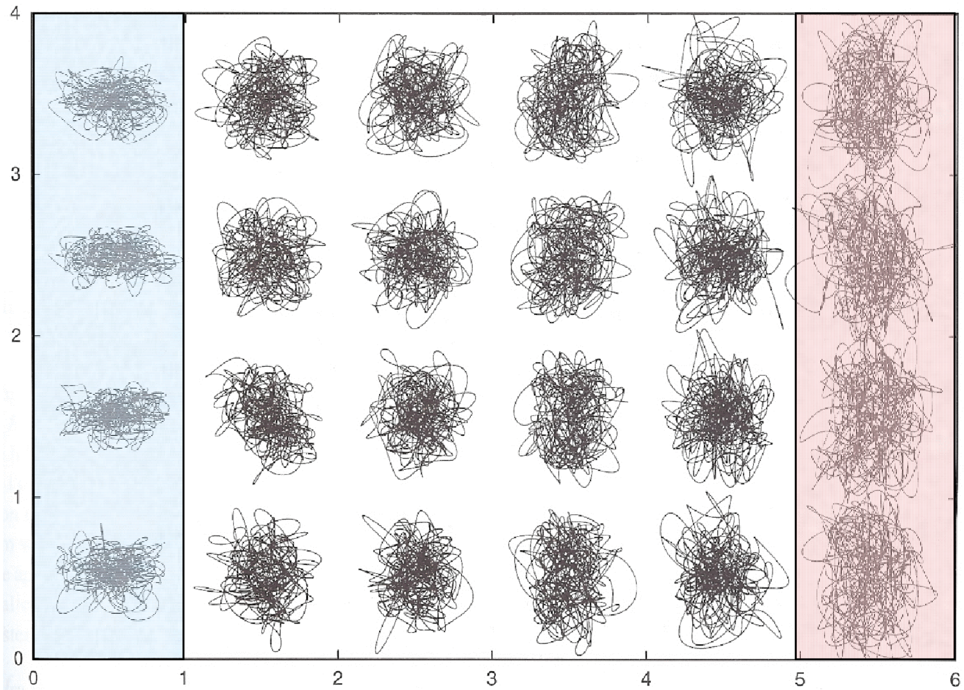


In two Dimensions there can be a Substantial * Dimensionality Loss !

* Europhysics Letters (2002) ; S_{Gibbs} → minus infinity !

Heat Conduction in 2D ϕ^4 Slab

$$\Phi_{\mathrm{Newton}} = \sum_{\mathrm{sites}} \delta^4/4 + \sum_{\mathrm{pairs}} \left(|r|-1\right)^2/2 \,.$$



Hoover, Aoki, Hoover, and De Groot Physica D (2004)

Four COLD Particles + Four HOT Particles

ϕ^4 → Dimensionality Reduction

Thermostated Equations of Motion →

$$\dot{f}/f = -\dot{\otimes}/\otimes = +\Sigma\varsigma_i = -\Sigma\lambda_i = \dot{S}/k > 0 \Rightarrow$$

$[f \rightarrow \infty$ and $\otimes \rightarrow 0]$!

$$\dot{\otimes}_1/\otimes_1 = \lambda_1$$

$$\dot{\otimes}_2/\otimes_2 = \lambda_1 + \lambda_2$$

$$\dot{\otimes}_3/\otimes_3 = \lambda_1 + \lambda_2 + \lambda_3$$

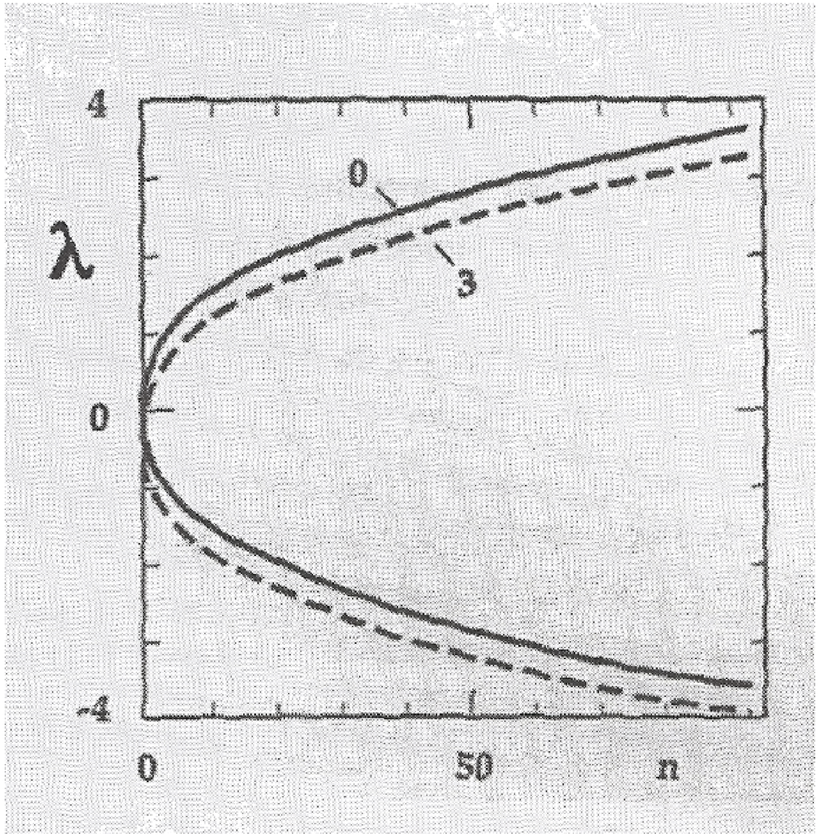
• • •

$$\dot{\otimes}_\#/\otimes_\# = \Sigma_i\lambda_i$$

Details follows from the "Lyapunov Spectrum" and imply the Second Law Of Thermodynamics .

Lyapunov Spectrum for N=32

Symmetry Breaking, for a Lennard-Jones Fluid * .

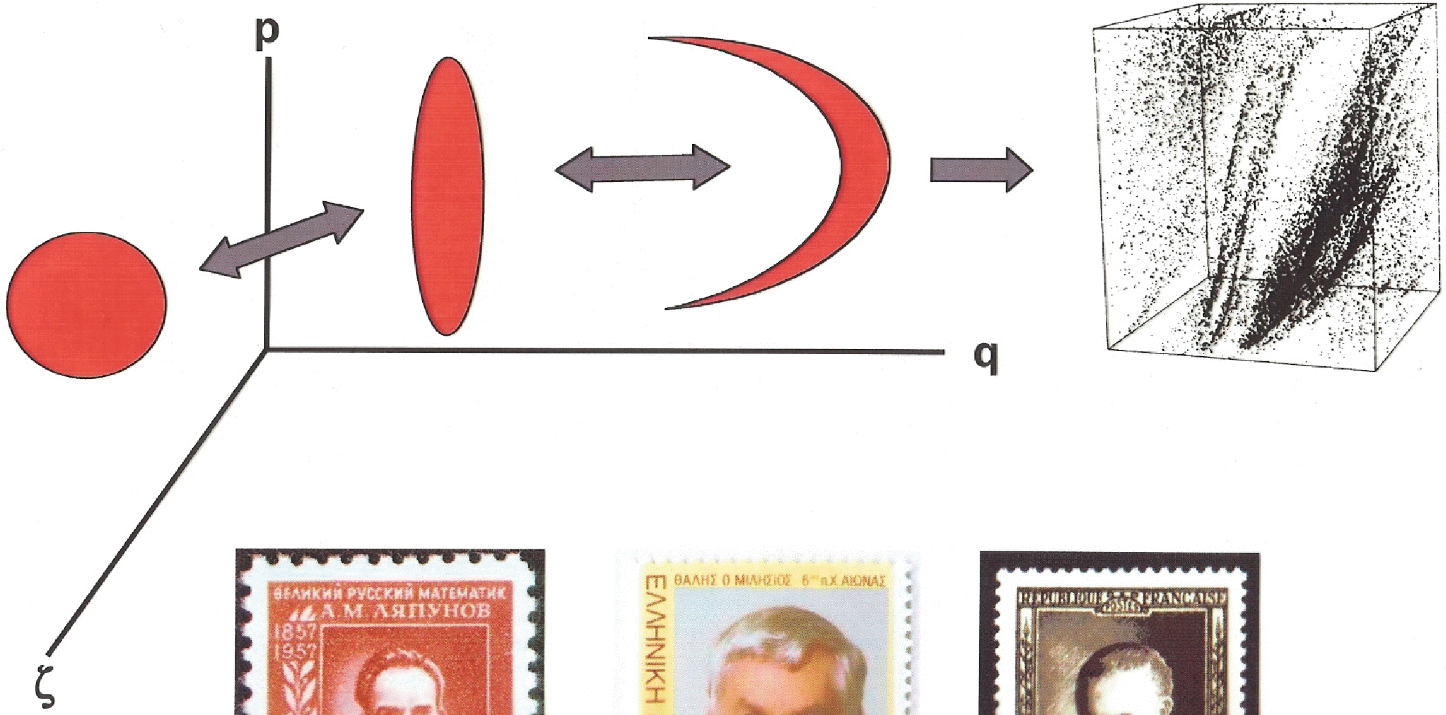


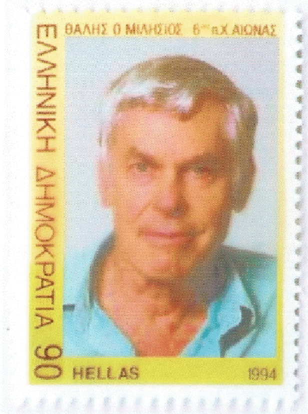
Time-Reversible Dynamics
Dissipative, dS/dt > 0 .
Zero Phase Volume
Multifractal Attractor
(with ΔD ~ 10)

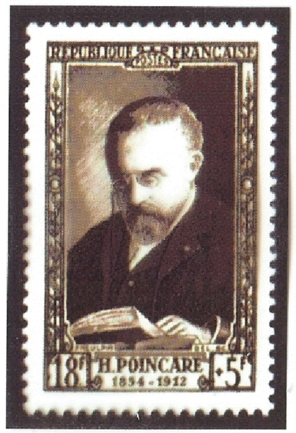
Thermostated Color Conductivity
16 Particles Pushed to the Right
16 Particles Pushed to the Left .

*** Posch and Hoover (1987) .**

Generic Nonequilibrium Phase Space Flow







SPAM → Continuum Mechanics

Particles can be used to solve Continuum Problems !

For Density ρ use Particle-centered weight functions .

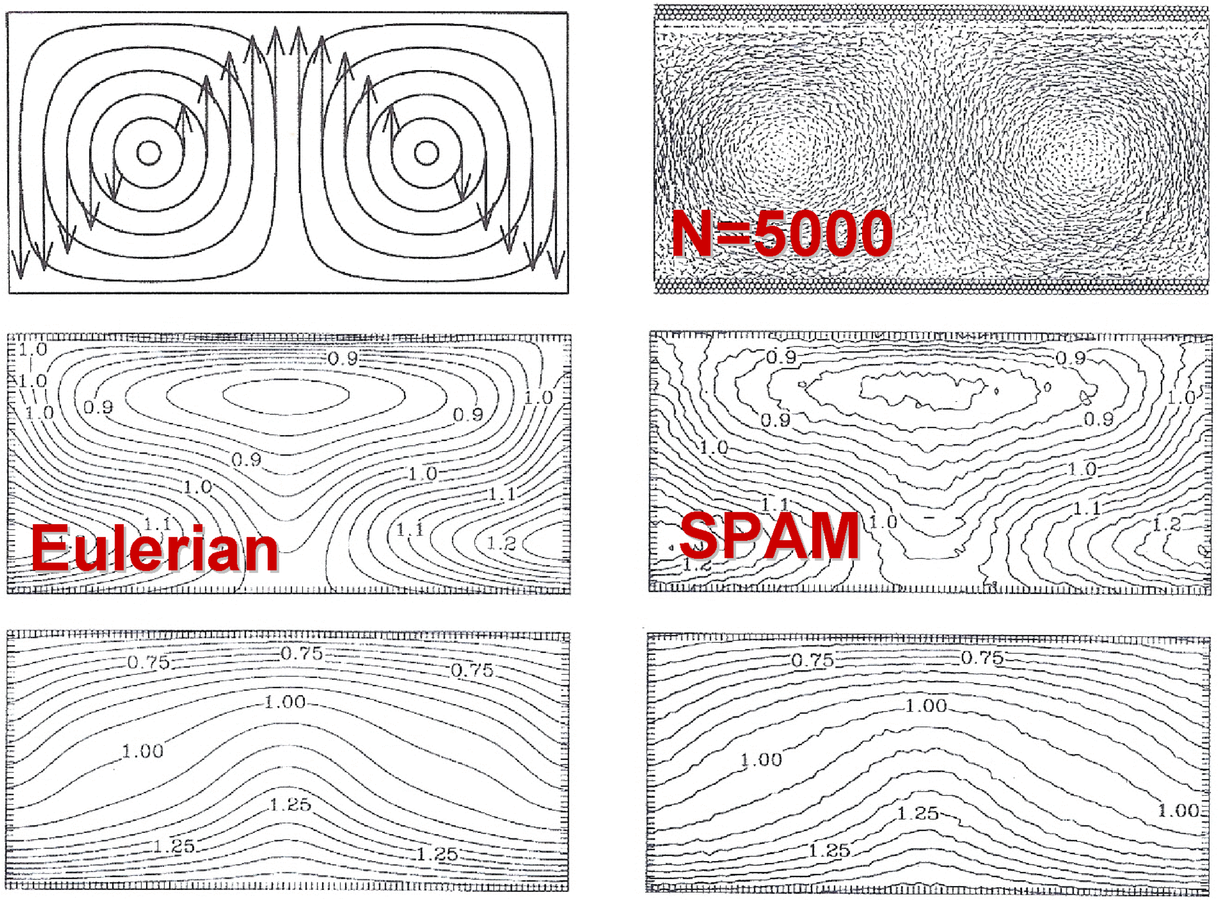
The Equations of Motion mimic Molecular Dynamics .

$$\rho(r) = \Sigma_j m_j w_{rj} \Rightarrow$$

$$\dot{v}_i \equiv -\Sigma_j[(P/\rho^2)_i + (P/\rho^2)_j] \bullet \nabla_i w_{ij}$$

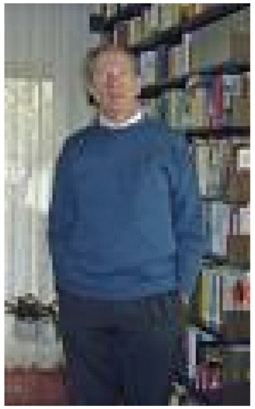
from $\dot{v} = -\nabla \bullet (P/\rho) - (P/\rho^2) \bullet \nabla\rho$.

Eulerian Continuum Mechanics Compared to SPAM [Particles]



ρ

T



5. Some Flies in the Ointment

Nonlinearity :

In strong shockwaves heat flows the “wrong” way .
In strong shockwaves the viscosity is increased .

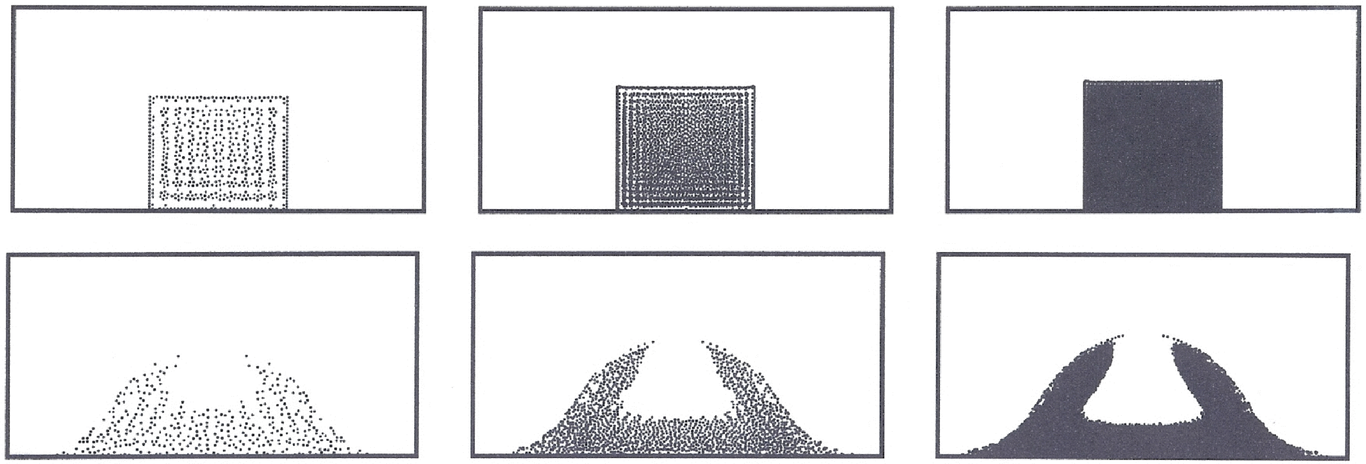
The shockwave problem is well suited to investigation because the boundary conditions are equilibrium states .

Rotation :

The evolution of stress (Jaumann stress) is a classic Difficulty in Continuum Mechanics. There is an analog In judging what “comoving” (corotating ?) means in Nonequilibrium Molecular Dynamics’ shear flows .

5. Fracture, Failure, Damage

Reliable Formulations of Failure Needed* .
Energy, stress, plastic strain are usable .
Fluid & Solid models are easy to validate .



* New Surfaces, Porosity, Texture, Shearbands, Ductile *versus* Brittle .

5. Quantum Dynamics

There is much to do, but with a few clues:

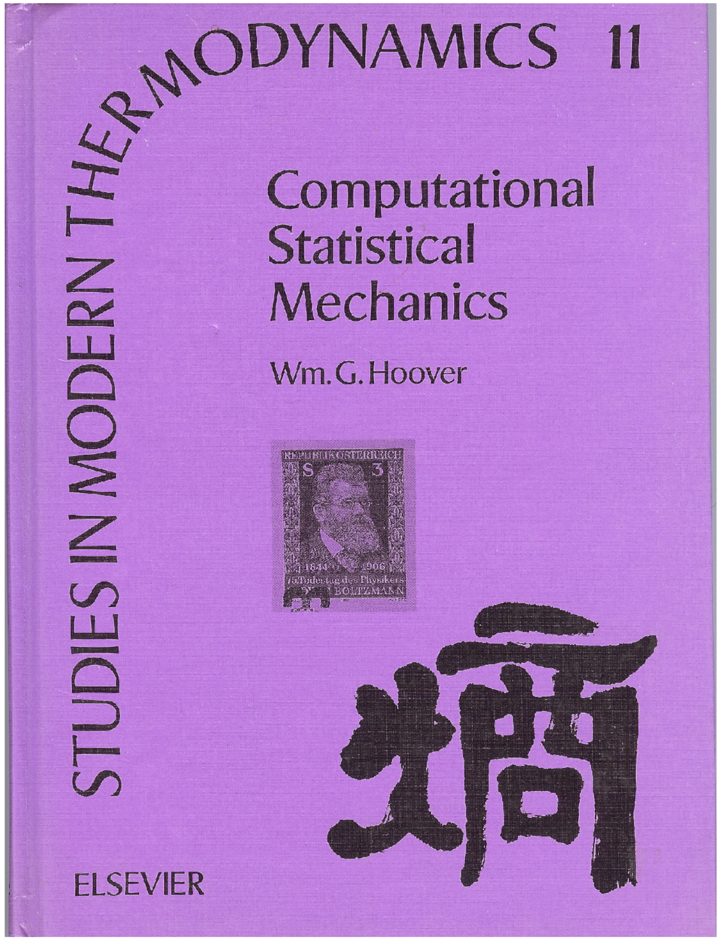
Hard spheres appear bigger, by λ .

Thermodynamics in powers of h , which led to the configurational T expression .

Transport is in fractional (!) powers of h * .

* Bernard Jancovici, Physical Review (1969) ;
Bhuduri, van Dijk, Srivastava, 13 July 2006 arXiv .

Some Useful Reference Books



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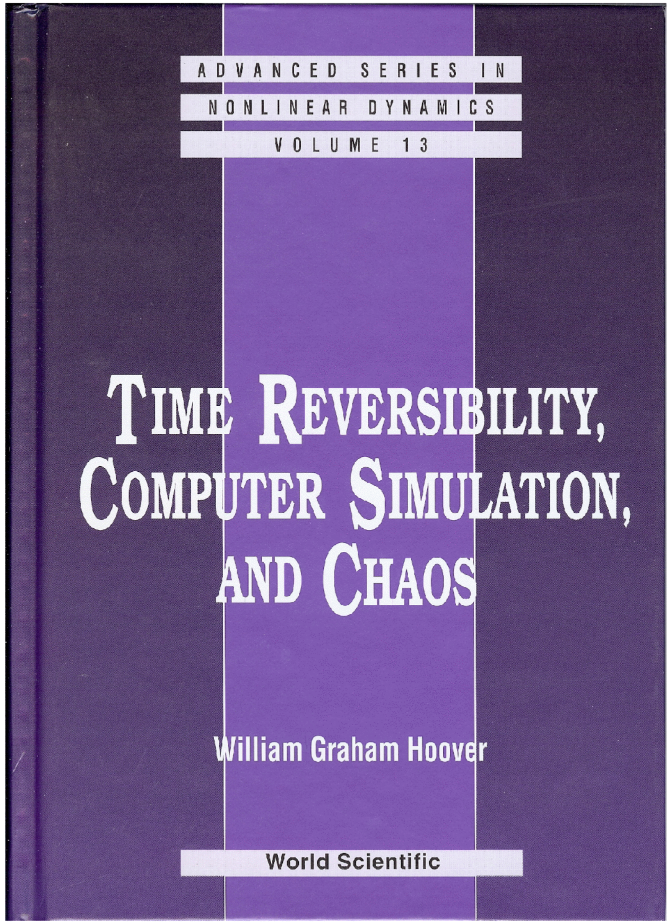

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