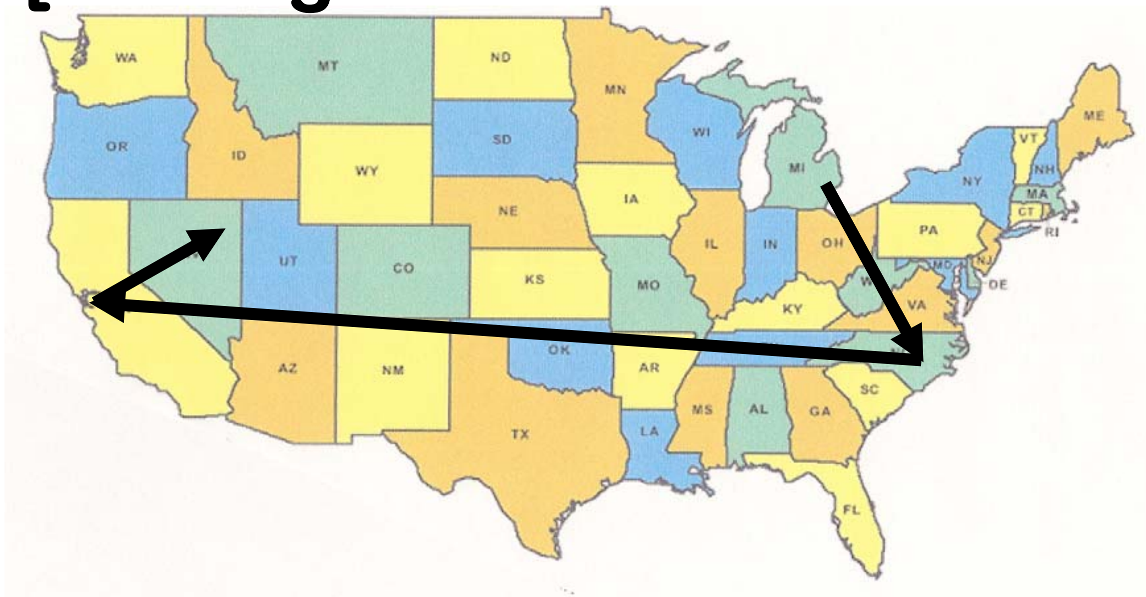
Nonequilibrium Molecular Dynamics

Wm G Hoover & Carol G Hoover
[no longer at UCDavis & LLNL!]

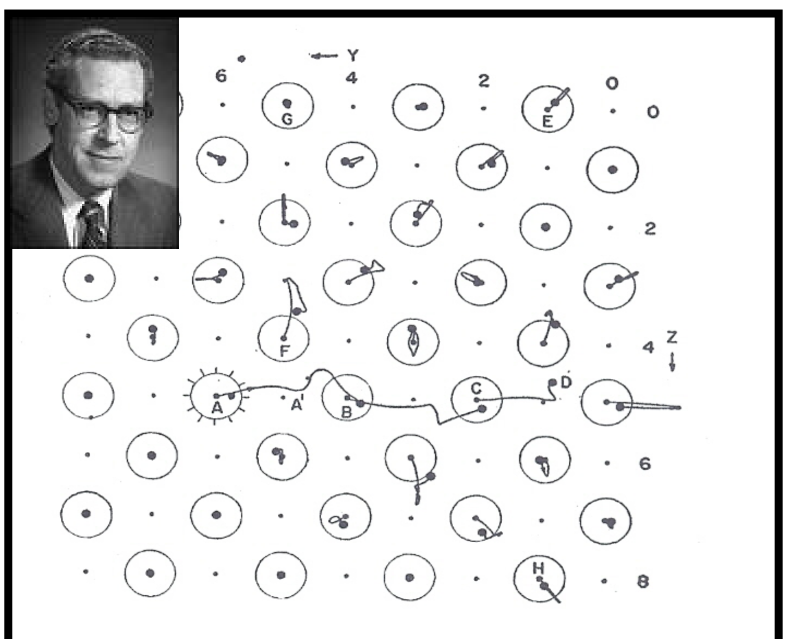


Foundations of Nonequilibrium Statistical Physics @ La Herradura, 13 September 2010

For details: http://williamhoover.info

Historical/AutoBiographical Summary

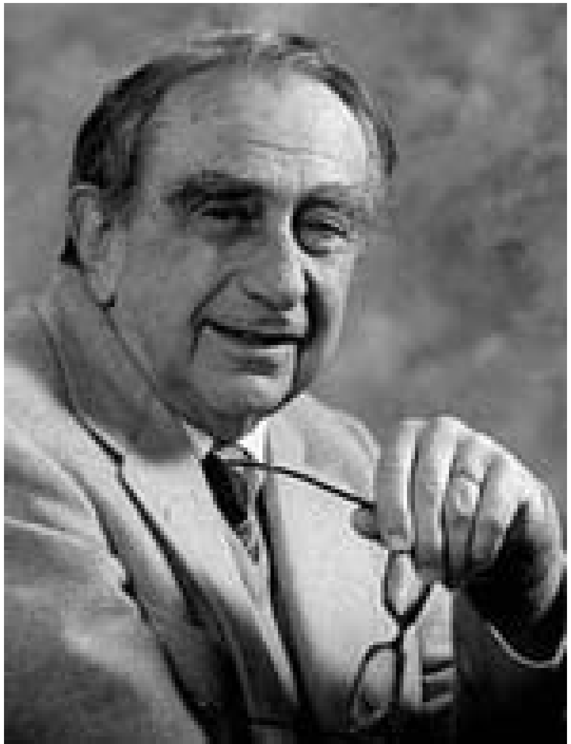
@ University of Michigan 1958-1961 and saw “Molecules in Motion” by Berni Alder & Tom Wainwright Scientific American (1959) .



Scanned at the American Institute of Physics

Historical/AutoBiographical Summary

@ Lawence Livermore Laboratory & "Teller Tech" [UCDavis] 1962-2004 [10,000 people/square mile]



Historical/AutoBiographical Summary

Bill Ashurst [PhD Thesis UCDavis 1972-1975] :
“Nonequilibrium Molecular Dynamics”

Systems far from Equilibrium [SPAIN 1980]

Shuichi Nosé [PARIS 1984 and JAPAN 1989]

Historical/AutoBiographical Summary

Retirement @ Ruby Valley, Nevada 2004

Nonequilibrium Molecular Dynamics

1. Goals: Understanding Flows, Failure, Instability .
2. Method: Scope and Ingredients .
3. Macroscopic Field Variables from Particles' {q,p} .
4. Examples of Linear and Nonlinear Transport .
5. **5.** Lyapunov Instability and the Second Law .
6. Remaining Puzzles and Good Problem Areas .

[For details see http://williamhoover.info]

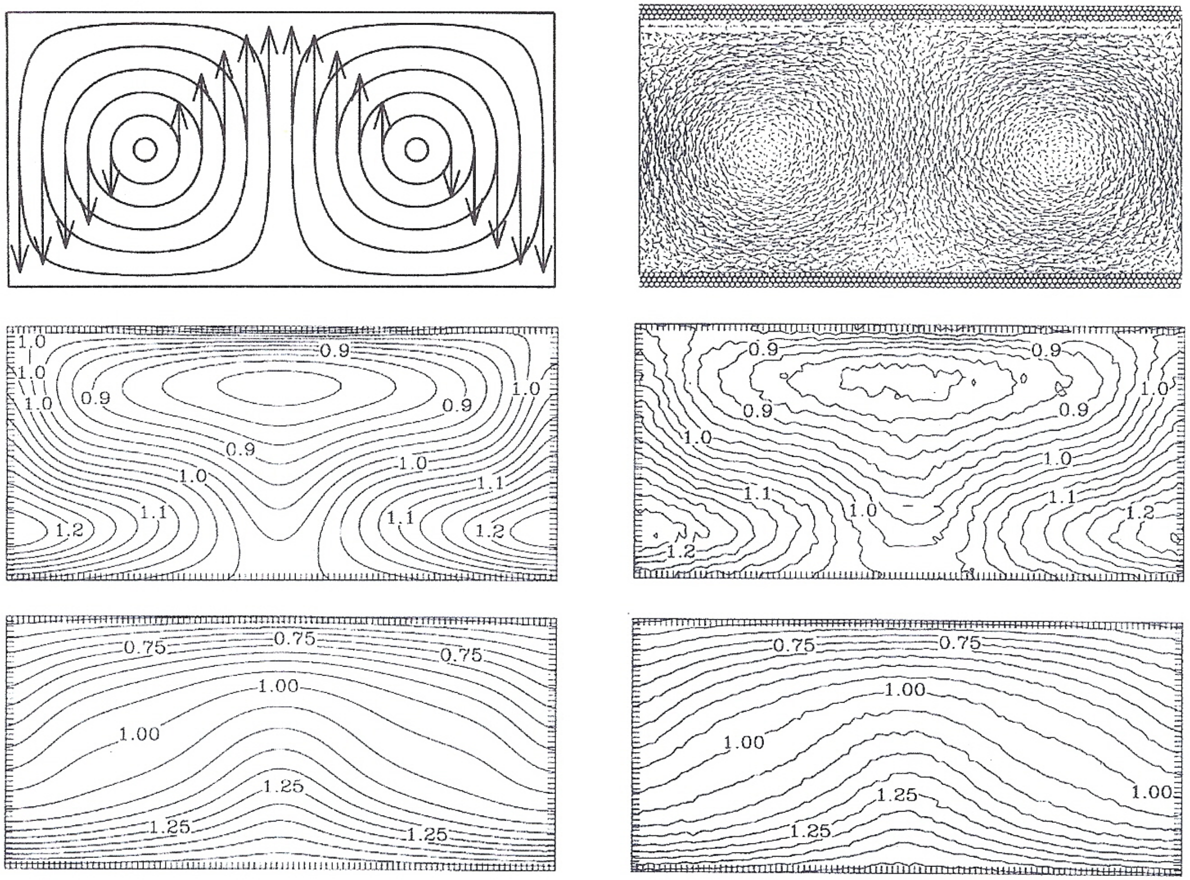
1. What NEMD is, and its Goals

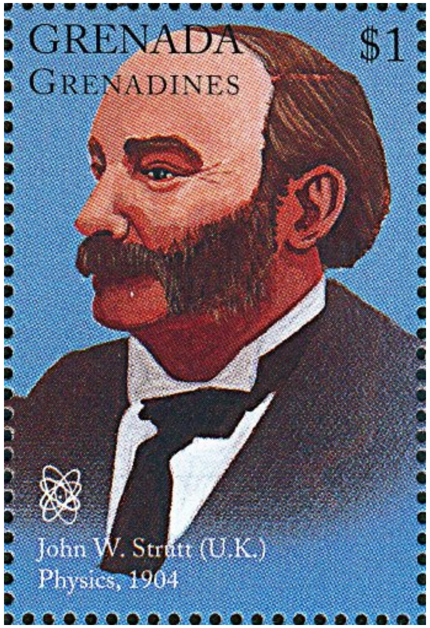
Atomistic Simulations of nonequilibrium systems, particularly steady states* :

$$\{ md^2r/dt^2 = F_A + F_B + F_C + F_D \}$$

* We control variables like { u, T, P, Q } .

1. Goals: Understanding Complex Flows



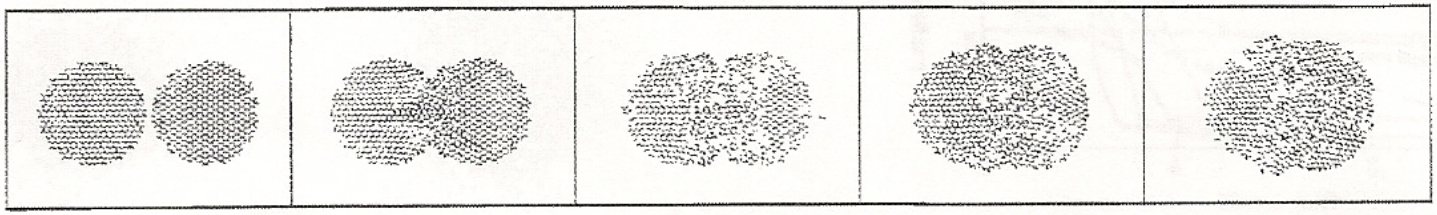


←N = 5000

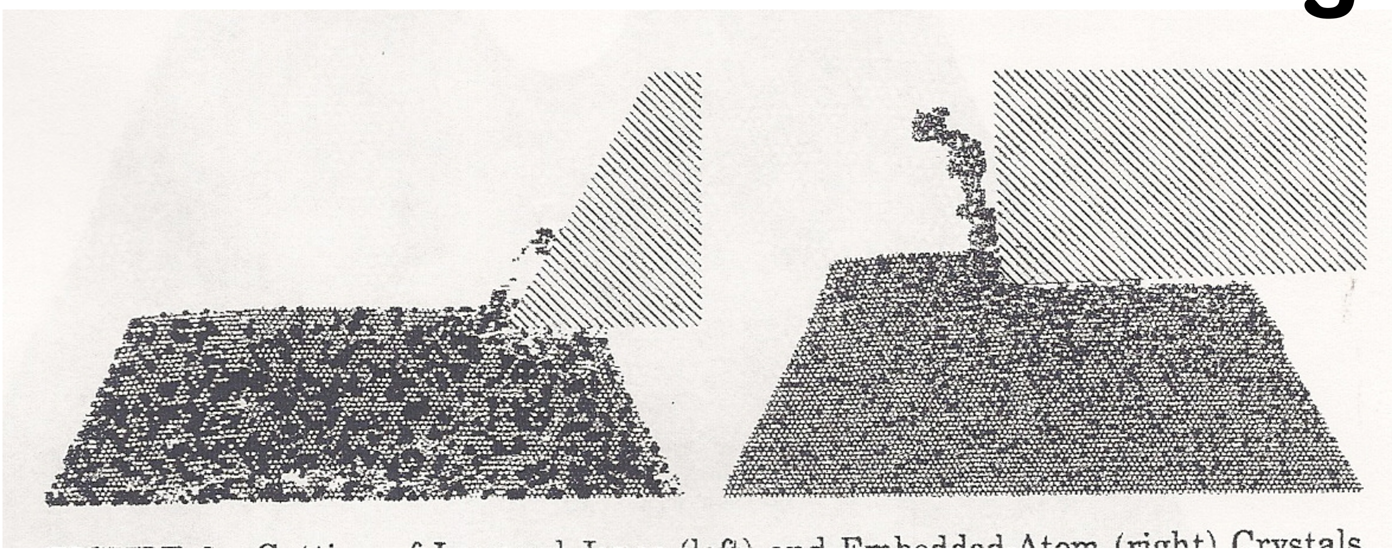
0.5 < T < 1.5

Continuum Mechanics *versus* SPAM, from Oyeon Kum's Thesis .

1. Goals: Failure and Instability

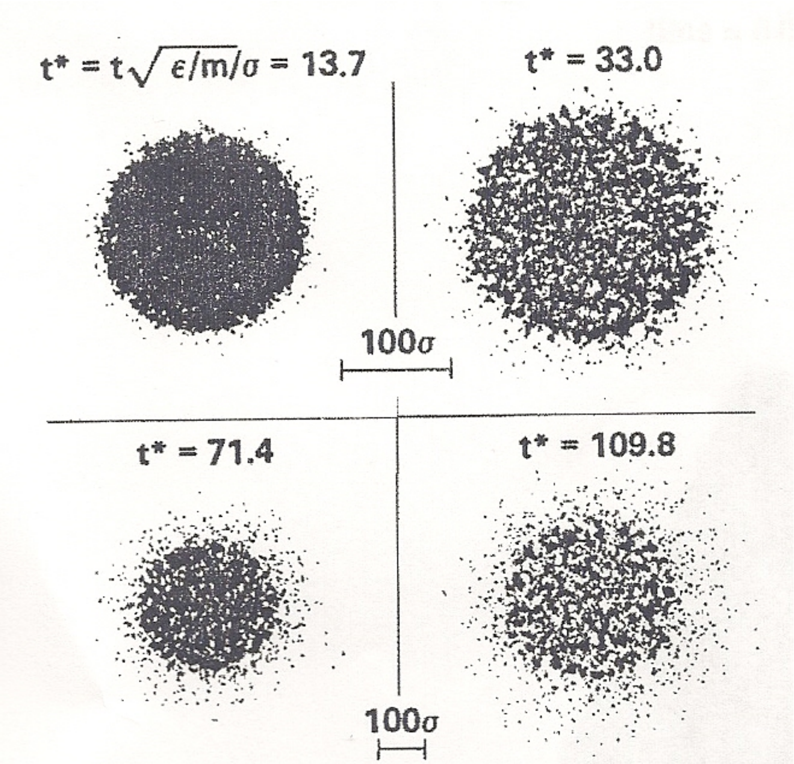


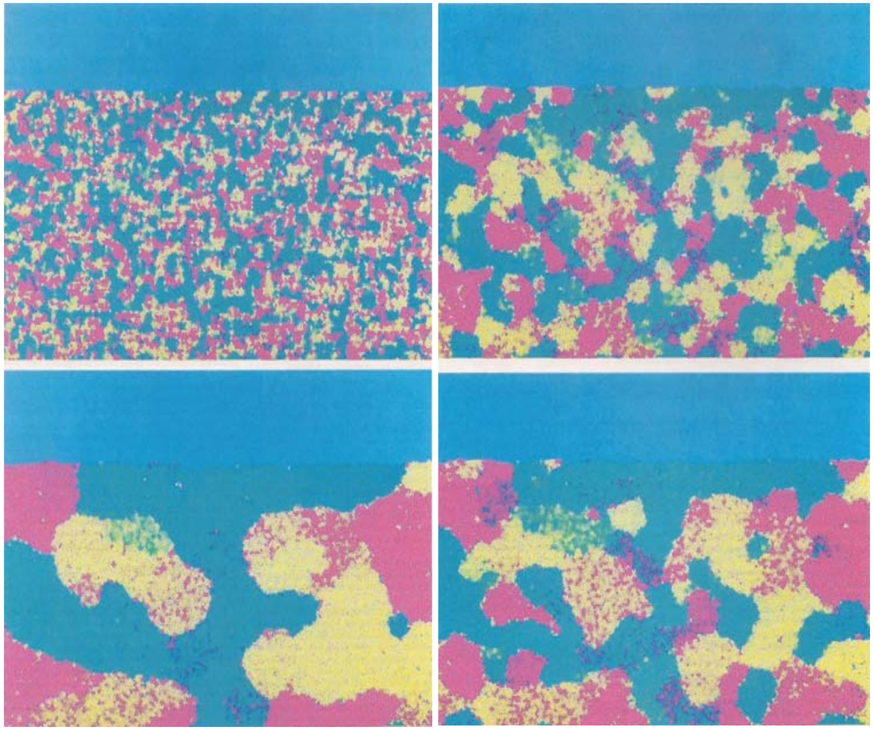
Restitution → Cold Welding



Thermostated Metal Cutting

1. Goals: Failure and Instability





[Fragmentation and Annealing]

2. Method: Scope and Ingredients

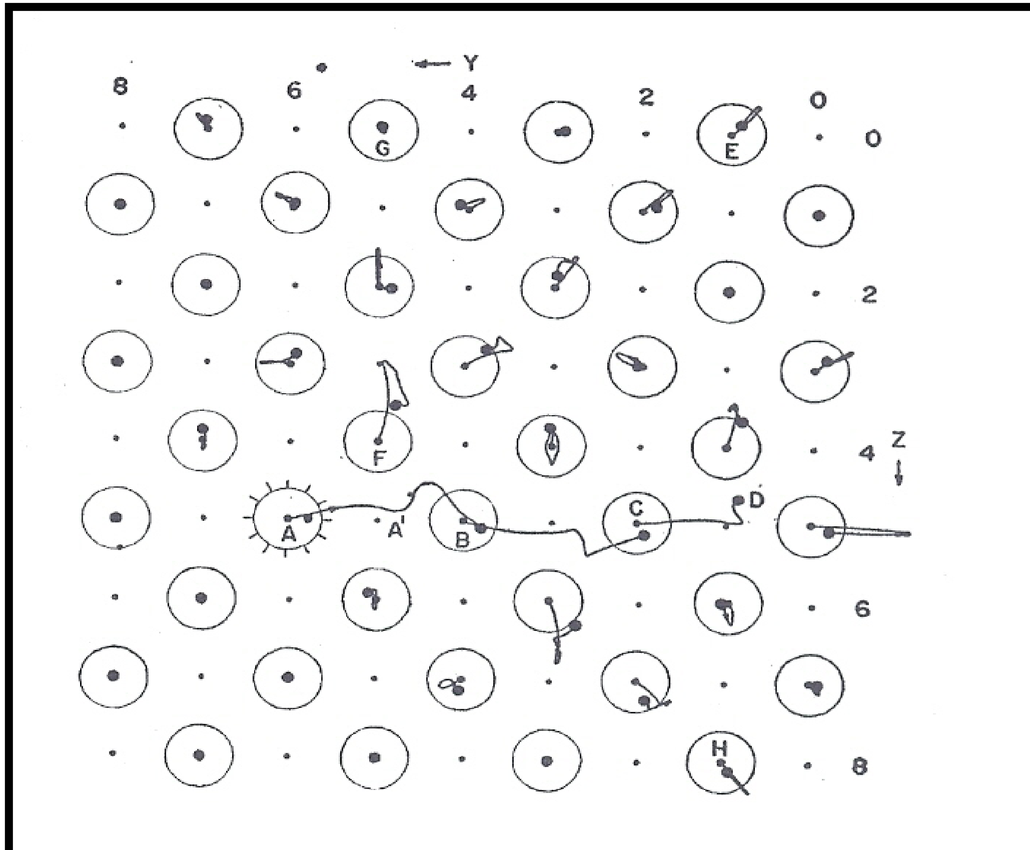
Simulations Solve Ordinary Differential Equations .

Use Runge-Kutta for as many as 10^{12} Equations .

$$\{ m d^2 r/dt^2 = F_A + F_B + F_C + F_D \}$$

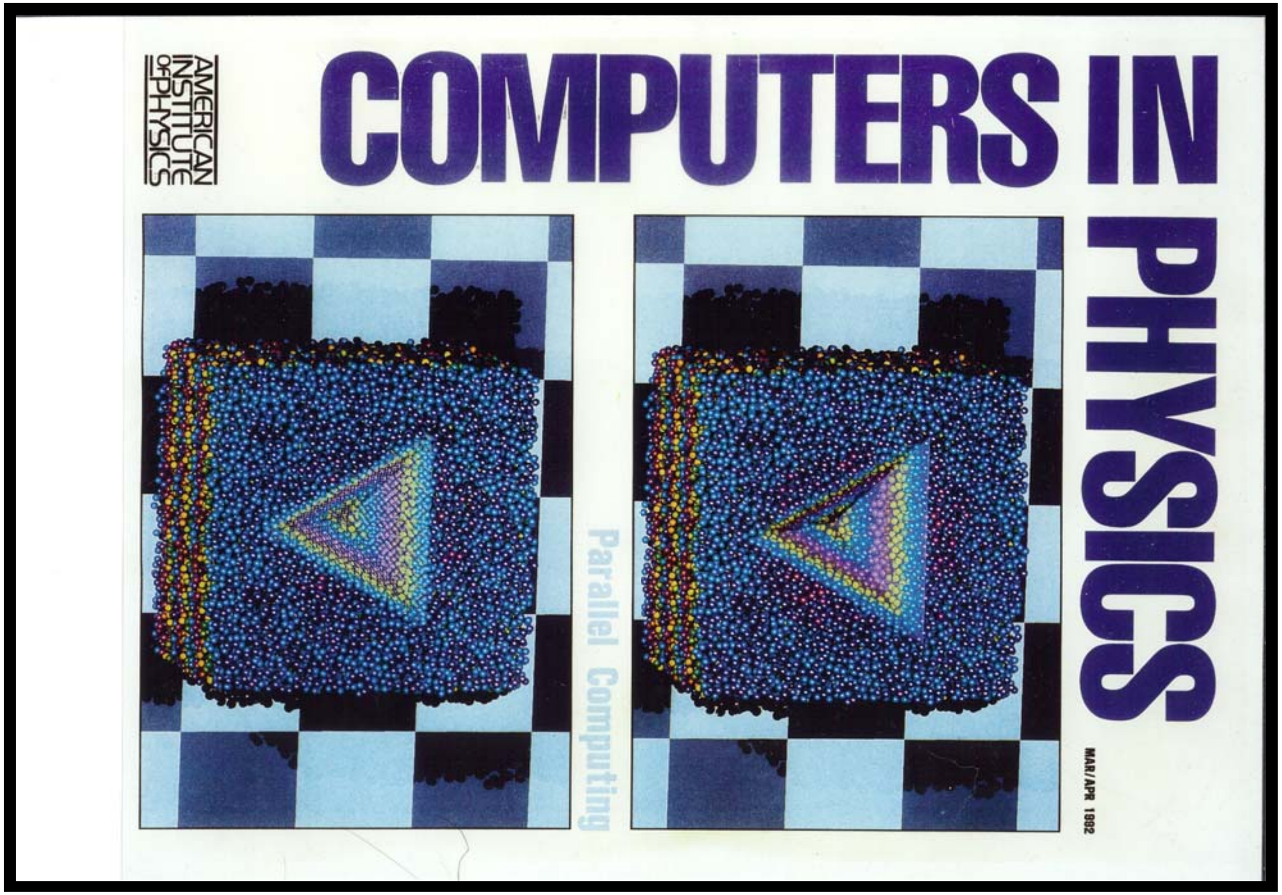
Formulate hydrodynamic/thermodynamic variables for simulations, and for analysis .

1959: Dynamics with 500 Particles



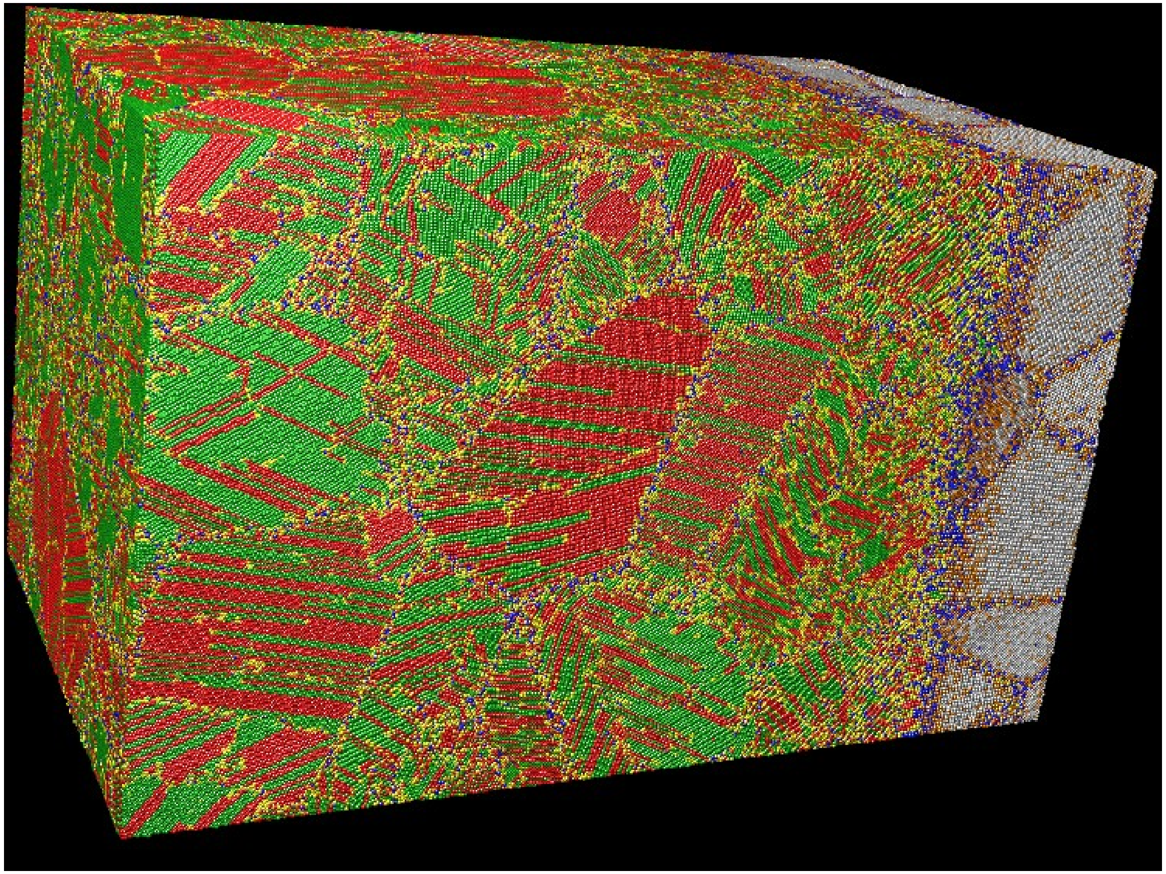
From Vineyard’s 1960 Physical Review Article

1989: Dynamics with 1,000,000 Particles



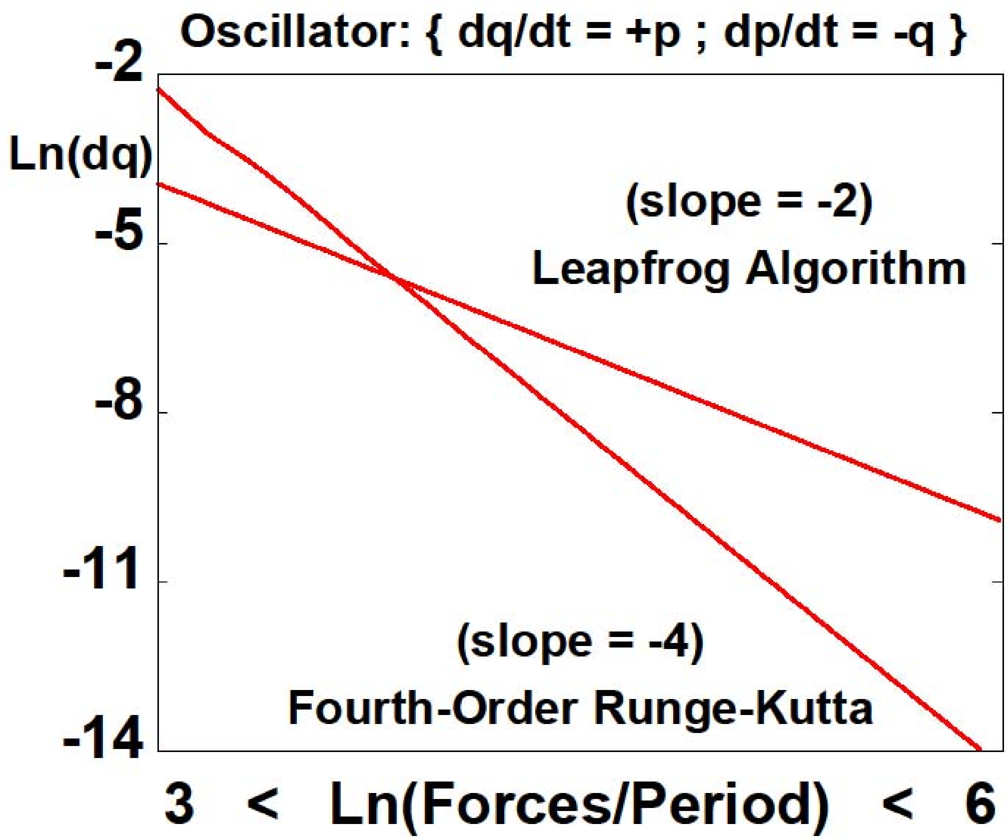
From our work in Japan, 1989-1990, simulating silicon .

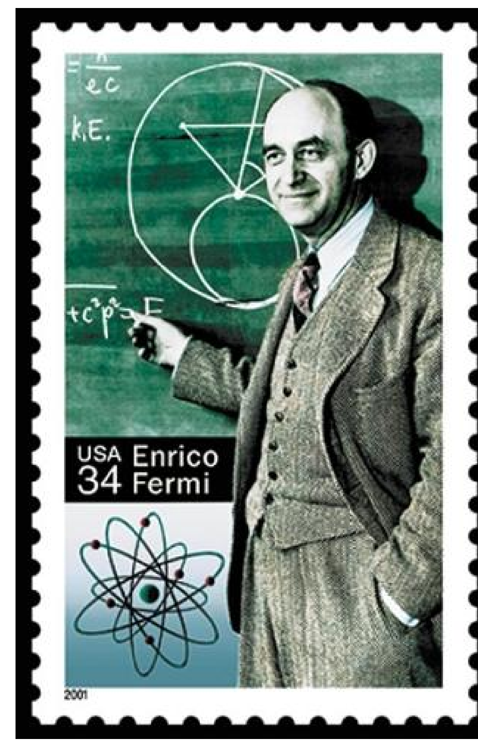
2007: Dynamics with 30,000,000 Particles



From Kai Kadau's Los Alamos Webpage

2. Methods: Leapfrog *versus* Runge-Kutta





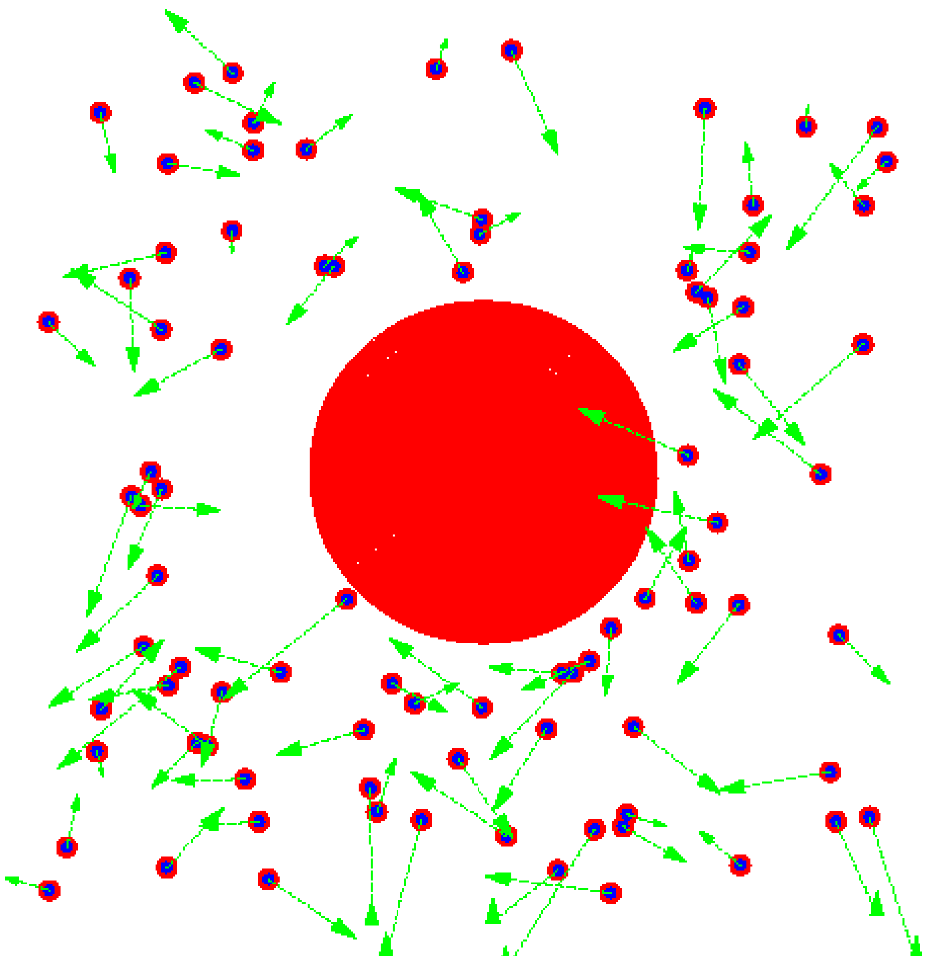
3. Microscopic → Macroscopic

For control and analysis of { u, T, P, Q } we need methods for defining point functions .

We describe atomistic dynamics in the Language of Continuum Mechanics .

3. Analysis from Kinetic Theory & Statistical Mechanics → T, P, Q .

Ideal Gas Thermometer



Temperature is just the *comoving* Kinetic Energy .

3. Nosé-Hoover Temperature Control

Dettmann's Hamiltonian $\mathcal{H}(q,p,kT)$:

$$\mathcal{H}(q,p) = s[K(p/s) + \Phi + \zeta^2\tau^2/2 + \#kT\ln s] = 0 \ !$$

Thermostated Oscillator Example :

$$H\ (q,p) = s[(q^2 + (p/s)^2 + p_s^2)/2 + \ln s] = 0 \ !$$

$$d^2q^2/dt^2 = -q - \zeta dq/dt \ ; \ d\zeta/dt = (dq/dt)^2 - 1 \ .$$

Nosé-Hoover equations maintain

Gibbs' Canonical Distribution !

3. Macroscopic Field Variables

$kT = \langle (p^2/m)_i \rangle$ **[*Comoving* p!]**

$PV = \Sigma(pp/m)_i + \Sigma(rF)_{ij}$

$E = \Sigma[(p^2/(2m)]_i + \Sigma\phi_{ij}$

$QV = \Sigma(pe/m)_i + \Sigma(rF\cdot p/m)_{ij}$

We need local definitions for all of these !

3. Molecular Dynamics → Continuum Mechanics

Long **MD simulations represent nanoseconds .**
Large **MD simulations represent microns .**
Continuum Mechanics uses Finite Elements rather than Atoms .

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

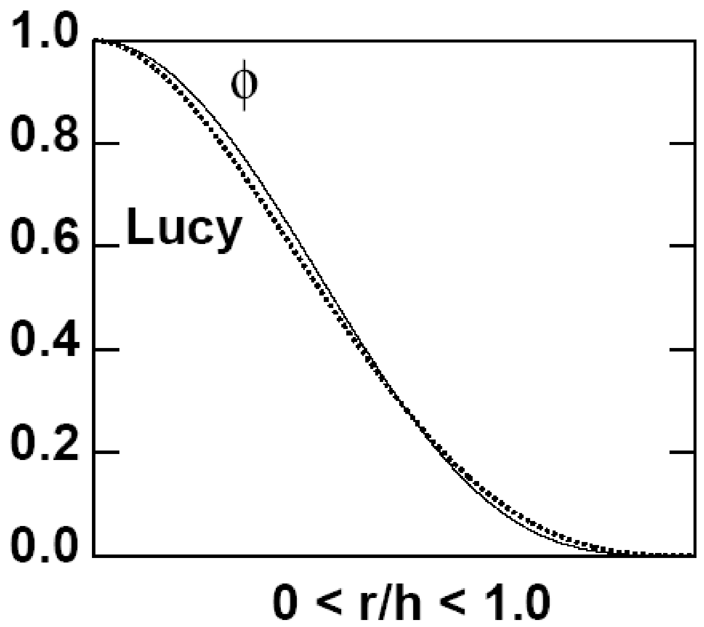
$$\rho \dot{\mathbf{v}} = -\nabla \bullet \mathbf{P} + \rho \mathbf{g}$$

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

Examples coming in the Next Lecture .

3. SPAM*, a method for continuum mechanics

→ Lucy's weight function, $w = 1 - 6r^2 + 8r^3 - 3r^4$.



Short-range repulsive potential, $\phi = (1 - r^2)^4$.

* Smooth Particle Applied Mechanics

3. Macroscopic Field Variables with Compact Weight Functions adapted from SPAM simulations :

$$\rho(r_0) = \Sigma_j w(|r_j - r_0|) \text{ with}$$

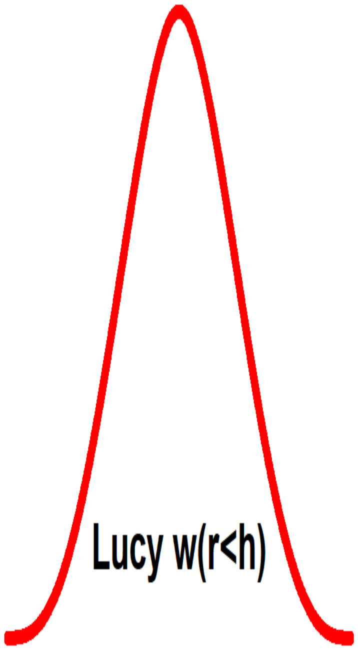
$$w_{1D} = C[1 - (r/h)]^3[1 + 3(r/h)]$$

$$C_{1D} = (5/4h)$$

$$C_{2D} = (5/\pi h^2)$$

$$C_{3D} = (105/16\pi h^3)$$

h = 3 is a good choice!



3. Macroscopic Field Variables ← Particles

The "Smooth Particle weight function" $w(r<h)$ smoothes out the particles over a range h, providing twice-differentiable density ρ, stream velocity u, *et cetera* .

$$\rho(\mathbf{r}) = \Sigma m_J w(\mathbf{r} - \mathbf{r}_J) \; ; \; \rho_I = \Sigma m_J w(\mathbf{r}_i - \mathbf{r}_J) \; ;$$

$$\rho(\mathbf{r})\mathbf{u}(\mathbf{r}) = \Sigma m_J v_J w(\mathbf{r} - \mathbf{r}_J) \; ;$$

$$\rho(\mathbf{r})e(\mathbf{r}) = \Sigma m_J e_J w(\mathbf{r} - \mathbf{r}_J) \text{ , and so on .}$$

Notice → Continuity Equation is an Identity !

NEMD: 4. Nonlinear Transport

Atomistic Simulations of nonequilibrium systems, particularly steady states, provide details of Nonlinear transport :

$$P_{xx} \neq P_{yy} \text{ and } T_{xx} \neq T_{yy}$$

We control variables like { u, T, P, Q } .

4. Linear/Nonlinear Shears

Boundary Forces : Moving and Periodic .

Constraint Forces : Constant { u, T, e } .

Driving Forces : Homogeneous { Doll's or s'llod } or Inhomogeneous .

Analyses : Tensor Natures of P and T :

{ P_{xx}, P_{yy}, P_{zz} } and { T_{xx}, T_{yy}, T_{zz} }
all differ systematically in nonlinearity .

4. Linear/Nonlinear Shears

For Doll's or s'lloD :

$$\{ \dot{x} = \dot{\varepsilon} y + (p_x/m) \}$$

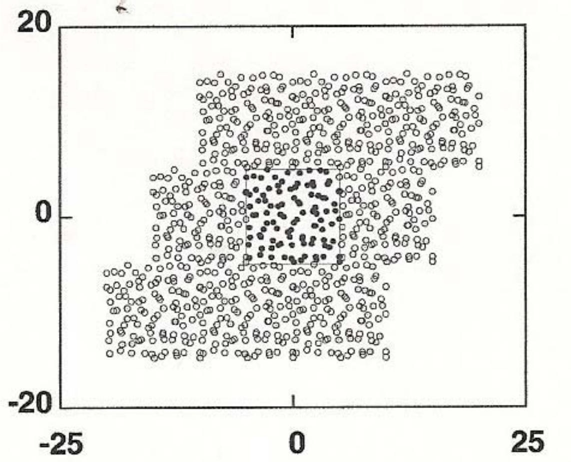
For Doll's Algorithm :

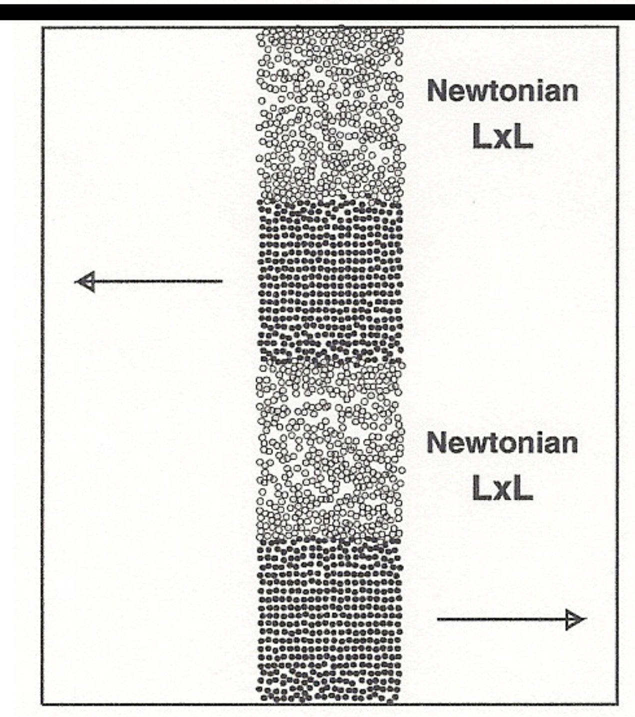
$$\{ \dot{p}_y = F_y - \dot{\varepsilon} p_x - \zeta p_y \}$$

For s'lloD Algorithm :

$$\{ \dot{p}_x = F_x - \dot{\varepsilon} p_y - \zeta p_x \}$$

4. Homogeneous *vs* Inhomogeneous Shears





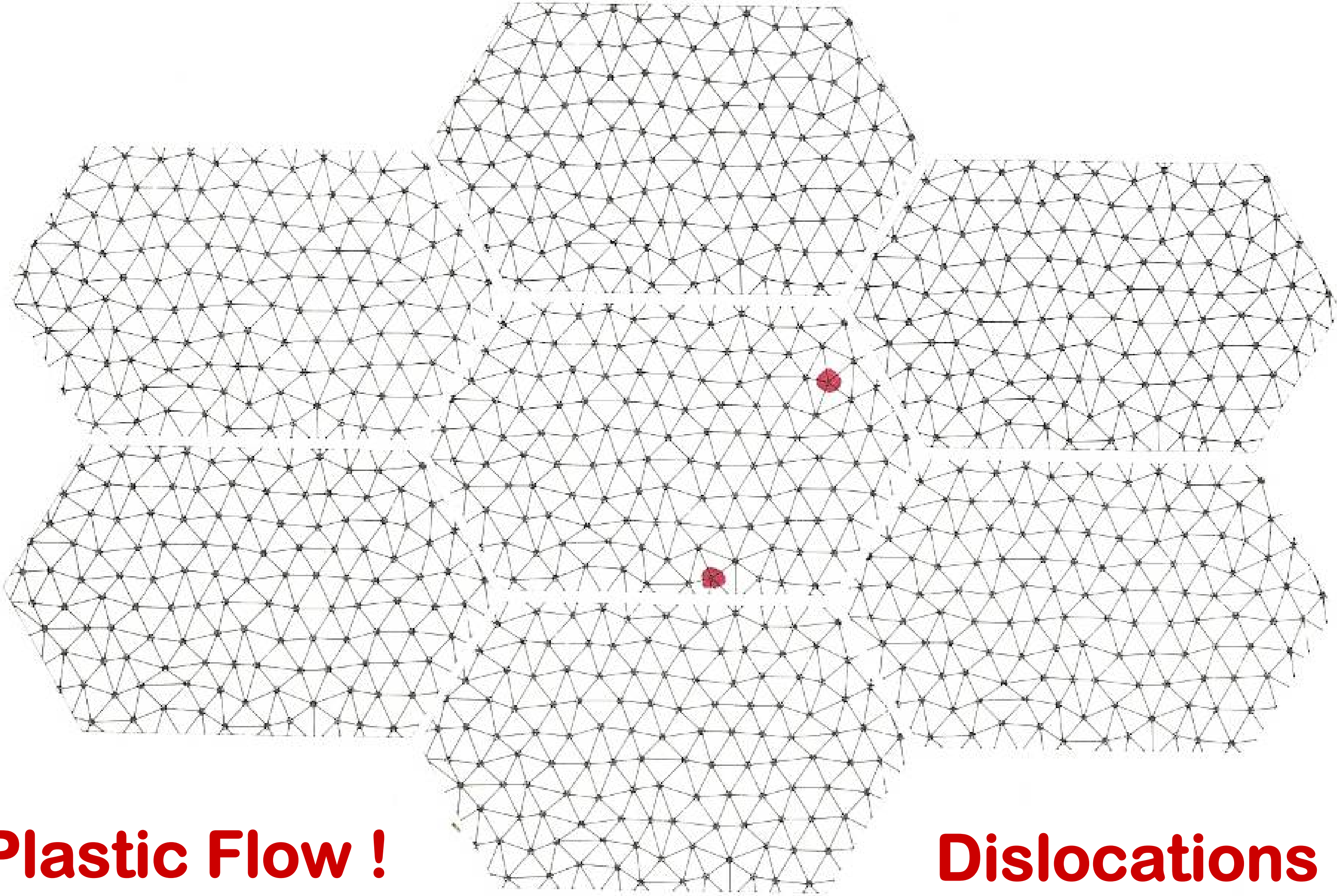
Tyy > Txx > Tzz
For Doll's

Txx > Tyy > Tzz
For s'lloD

$$T_{xx} > T_{zz} > T_{yy}$$

PRE 78, 046701 (2008)

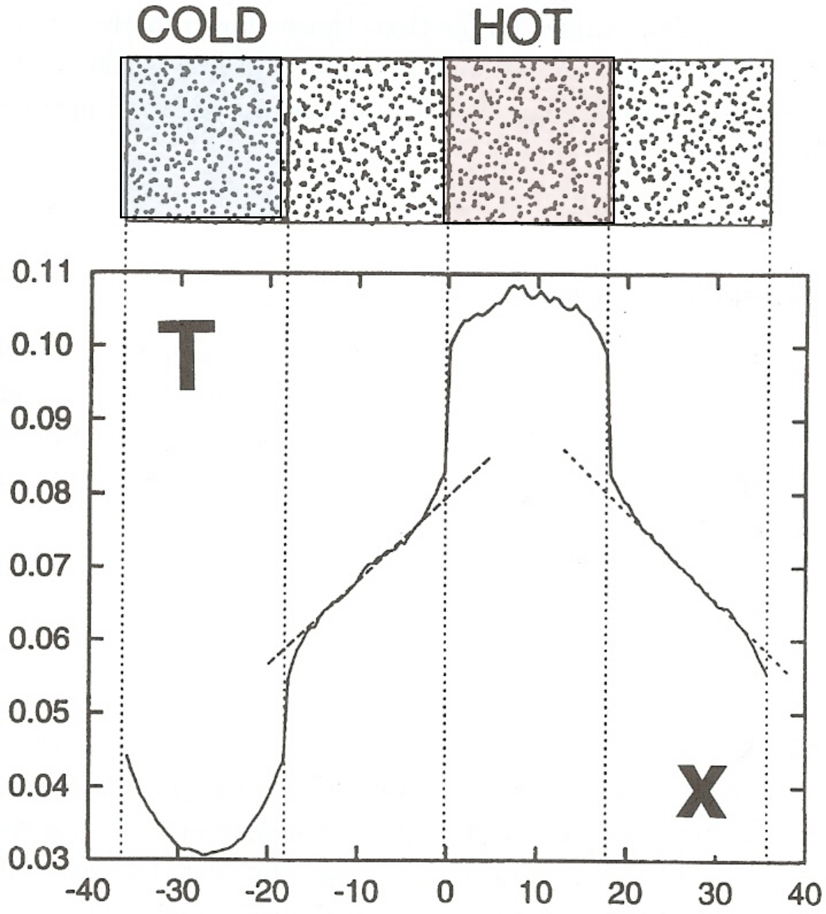
4. Periodic Solid-Phase Shear



Plastic Flow !

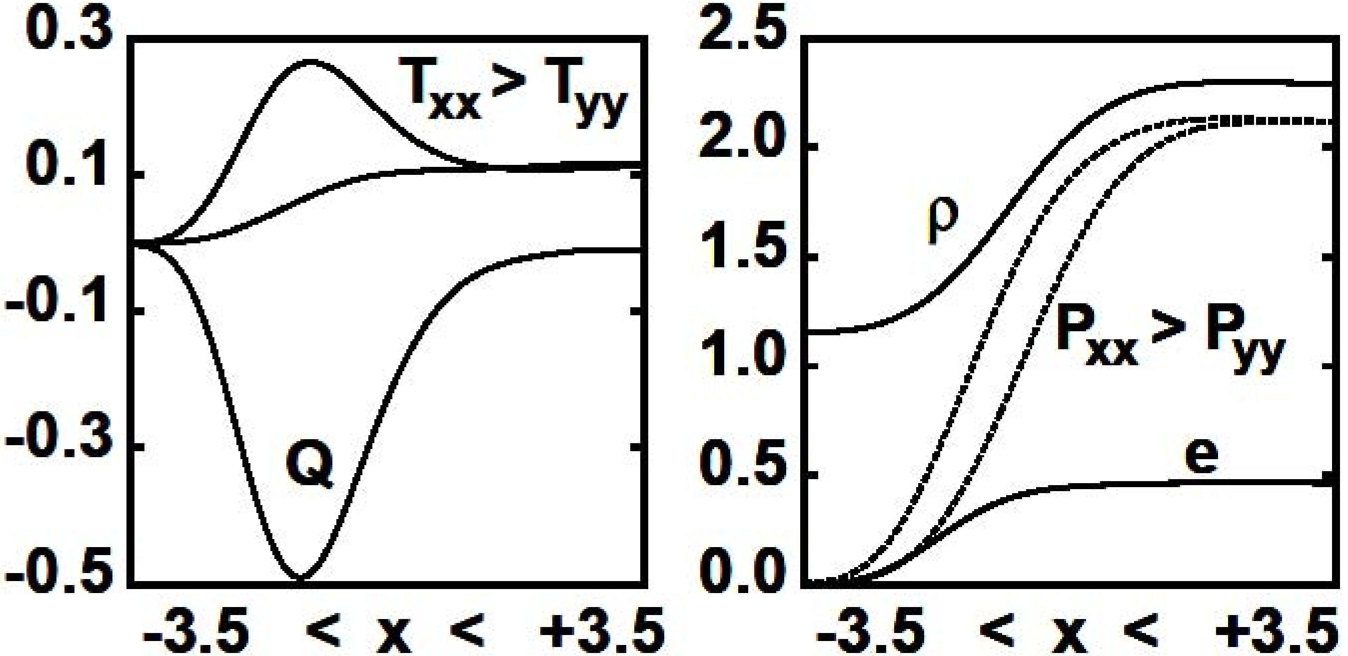
Dislocations !

4. Four-Chamber Periodic Heat Flow Problem



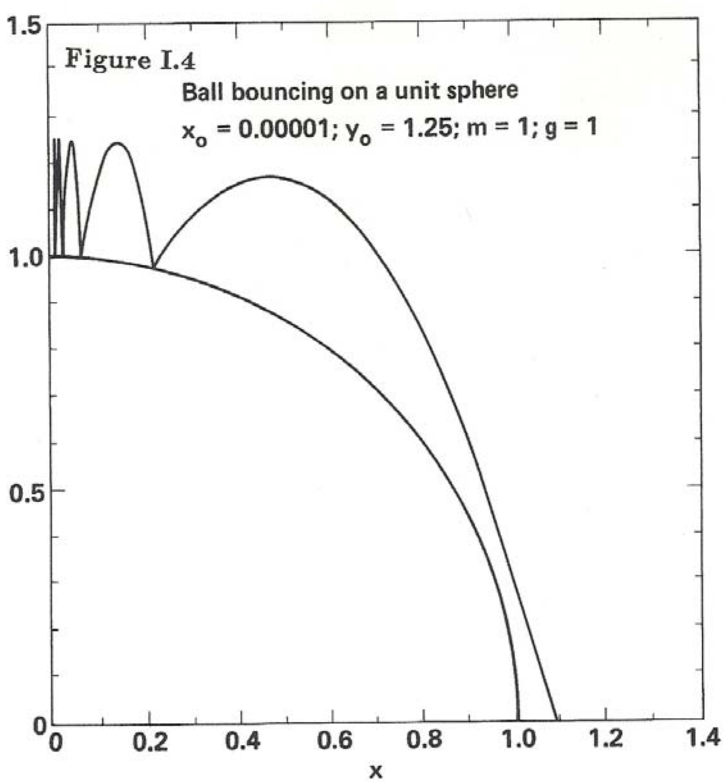
4. Molecular Dynamics → Shocks*

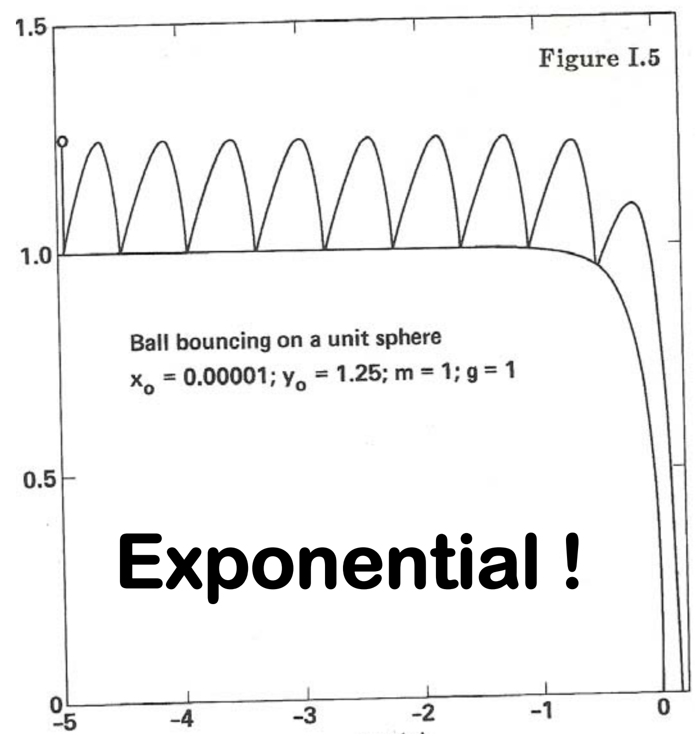
Molecular Dynamics Spatial Profiles
Lucy Averages Calculated with h = 3



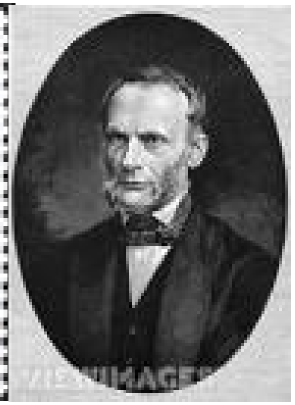
*** More Later !** **Details are in PRE (2010).**

5. Irreversibility-Lyapunov Spectra
Lyapunov Instability for a Ball





5. Second Law of Thermodynamics



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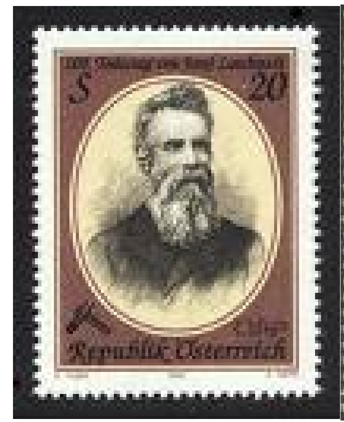
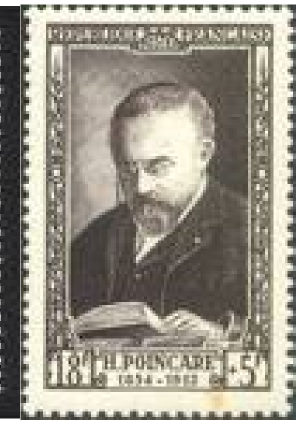
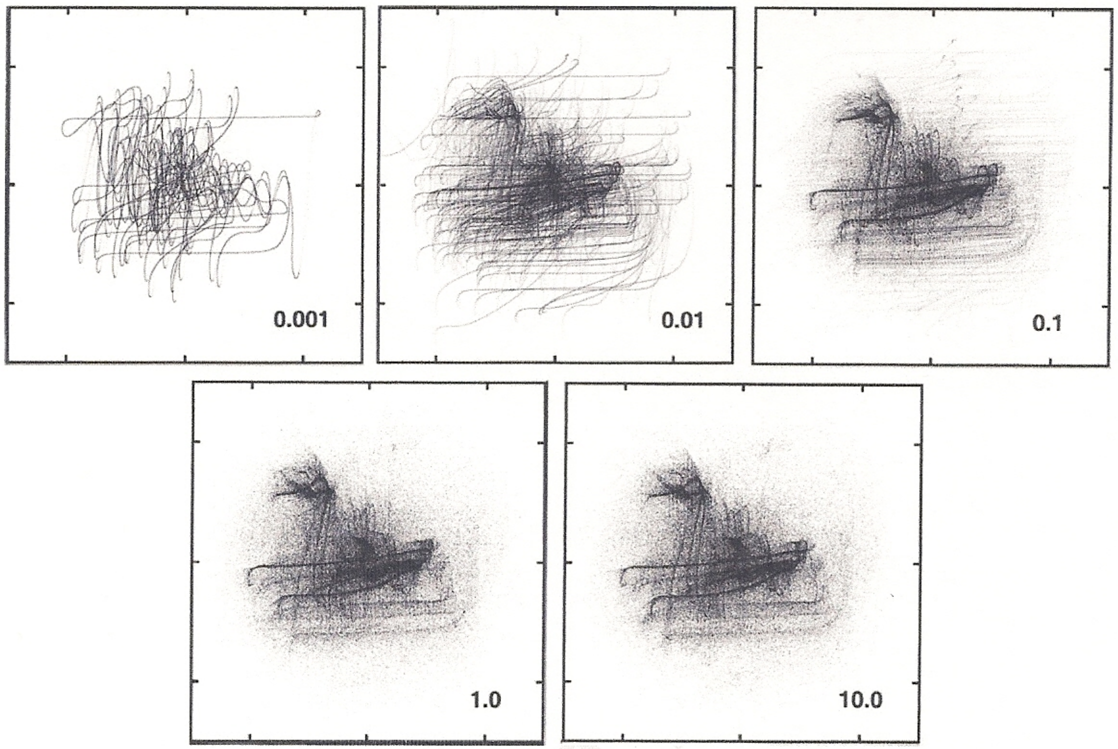




Boltzmann: Entropy Increases (Dilute Gases) .
Kelvin: Work to Heat is ok. *Not* the reverse !
Clausius: Entropy Increases !
Loschmidt: But the Equations are Reversible !
Poincaré: But the Initial Conditions Recur !

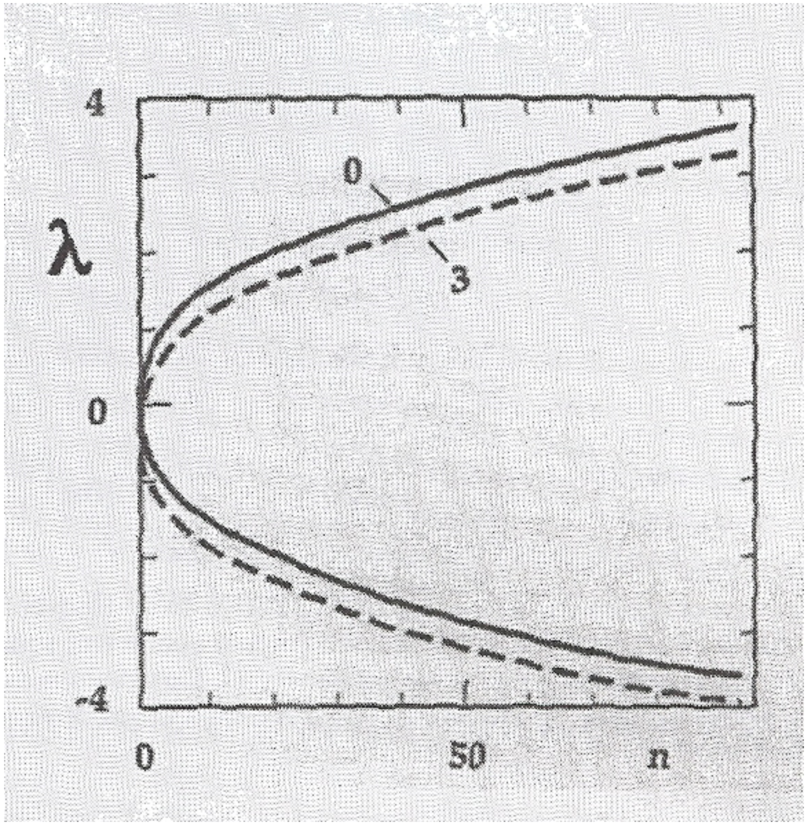
5. Fractal Formation for an Oscillator



Increasing the point-to-point time interval reveals a fractal distribution .

5. Lyapunov Spectrum for N = 32

Symmetry Breaking, Lennard-Jones Particles



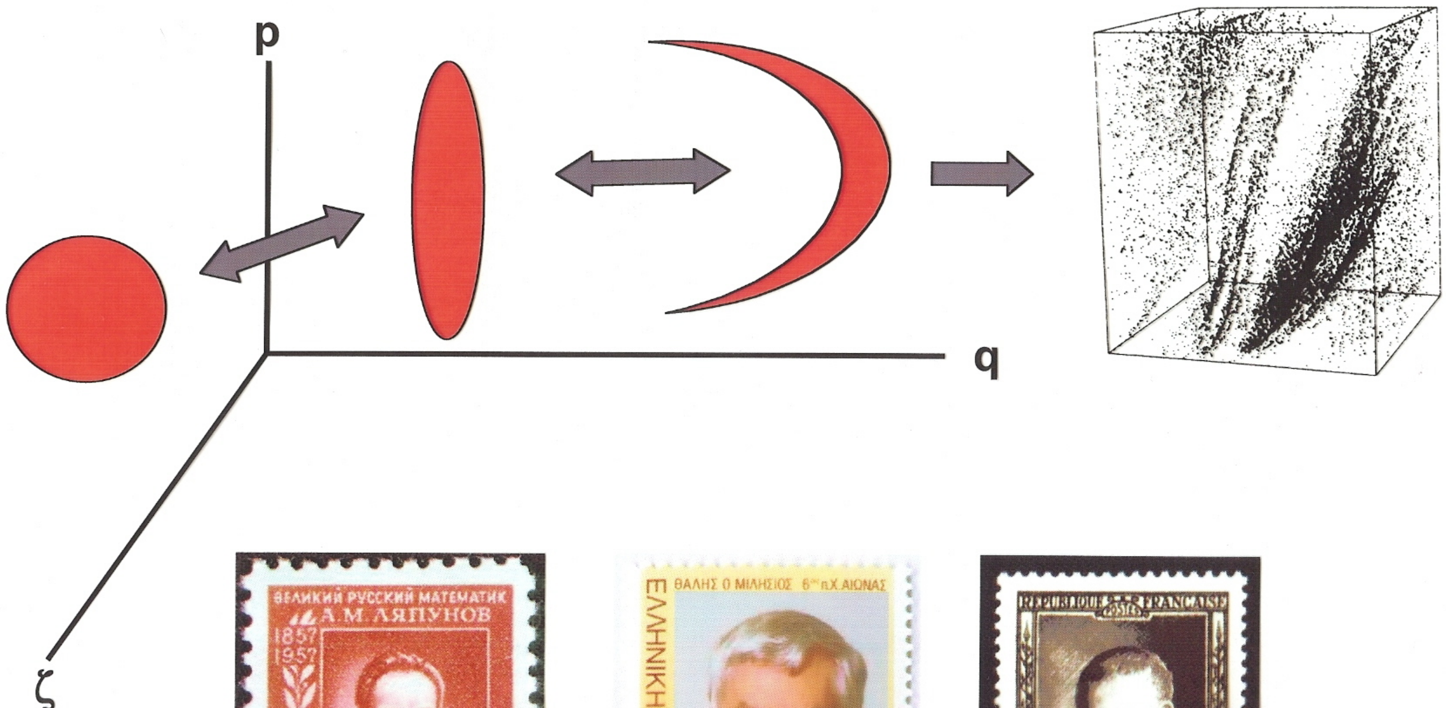
Time Reversible Dynamics
Dissipative, dS/dt > 0
Zero Phase Volume
Multifractal Attractor

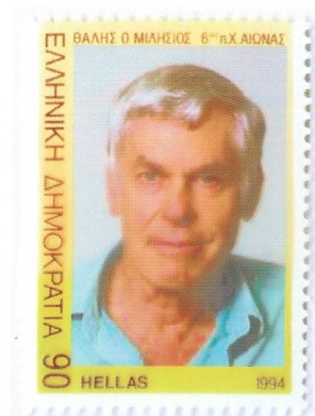
Thermostatted Color Conductivity
External Field in x Direction:
16 Particles Pushed to the Right
16 Particles Pushed to the Left

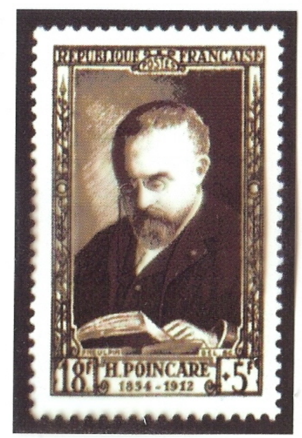
96 Pairs of λ → ΔD of order −10

Posch and Hoover, 1987

5. Generic Nonequilibrium Phase Space Flow







Fluctuation Theorem(s) describe this shrinkage .

5. Lessons from the Fractals

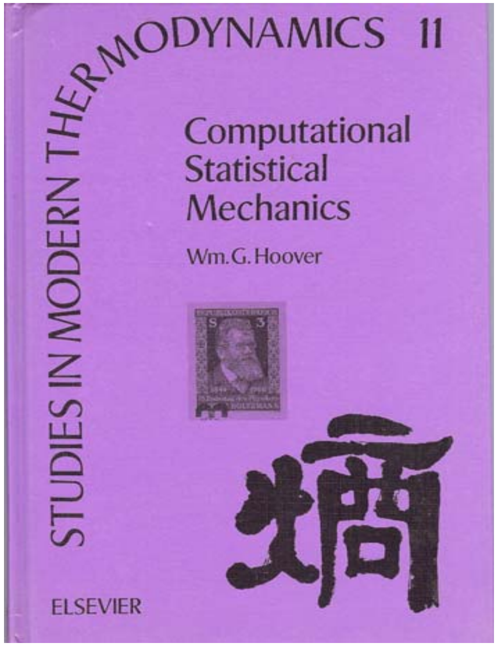
- Nonequilibrium States are very Rare .
- Comoving phase volume vanishes .
- Distributions’ Dimensionality Reduced .
- Distributions are Singular everywhere .
- Gibbs’ Entropy diverges to $-\infty$.
- Forward Stability > Backward Stability .

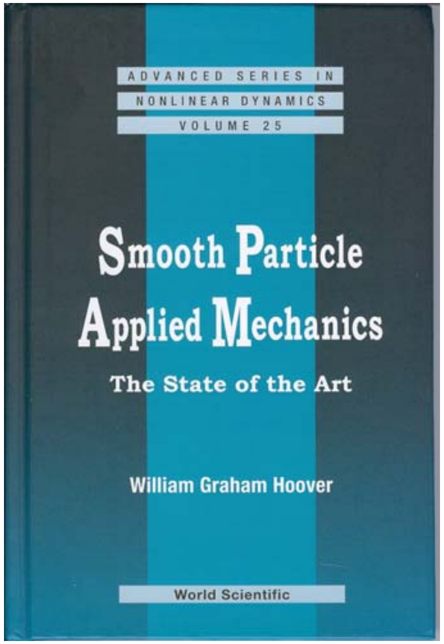
6. “What to do?” [Lenin]

Find the BEST method for defining Field Variables .

Analyze interesting problems with Local Lyapunov Spectrum, simplified with bit-reversible dynamics .

Develop two- and three-dimensional thermomechanics .





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