Kharagpur Lecture 6

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December 2016

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1. Gibbs' Canonical Thermodynamics

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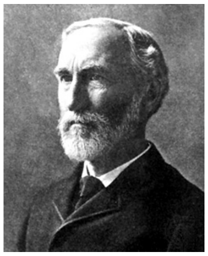
1. Gibbs' Canonical Thermodynamics (1902)



Gibbs related microscopic mechanics to macroscopic thermodynamics . We will explore the computational aspects of this connection including expansions in the density and inverse temperature . The fundamental basis of Gibbs' work is that all "states" are equally likely . Liouville's Theorem , the phase-space continuity equation , shows that this assumption is connected to Hamiltonian mechanics . In one dimension the continuity equation is $(\partial\rho/\partial t) = -(\partial(\rho v)/\partial x)$ and can be thought of as representing the conservation of mass or probability (or any other conserved quantity) .

Gibbs' microcanonical ensemble relates the entropy to the number of energy states . Because the probability of such states is proportional to the Boltzmann factor $e^{-E/kT}$ the properties of a system with a given (ideal-gas) temperature T are given by the canonical "partition function" Z *,

$$\Omega(E,V) = e^{[S/k]} = \#\text{ of E states ;}$$

$$e^{[S/k]}e^{[-E/kT]} = e^{[-A/kT]} \rightarrow$$

$$Z(V,T) = e^{[-A/kT]} = \prod \int\int [\, dqdp/h \,] e^{-[\mathcal{H}(q,p)/kT]}$$

* From the German "Zustandsumme" = state sum . A "Arbeit" [or "work"] is Helmholtz' Free Energy .

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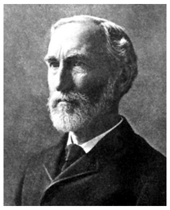
1. Gibbs' Canonical Thermodynamics (1902)



Gibbs' phase-space probability density is $f(q,p) = e^{-[\mathcal{H}(q,p)/kT]} / Z$.
If we average the logarithm $\langle \ln f \rangle = -(E/kT) + (A/kT) = (S/k)$.
(Remember that $Z = e^{-[A/kT]}$) .

Remember also Liouville's Theorem from Hamilton's motion equations :

$$(df/dt) = (\partial f/\partial t) + (dq/dt)(\partial f/\partial q) + (dp/dt)(\partial f/\partial p) =$$

$$-f[\,(\partial/\partial q)(dq/dt) + (\partial/\partial p)(dp/dt)\,] =$$

$$-f[\,(\partial/dq)(\partial H/\partial p) - (\partial/\partial p)(\partial H/\partial q)\,] = 0 \text{ .}$$

This seems like a very odd result , that the "entropy" is constant in any Hamiltonian flow . But it must be remembered that Gibbs' work applies to an "ensemble" of systems rather than the single system that is the subject of molecular dynamics. The entropy of a single system is not a well-defined concept without carrying out at least a time average .

Kharagpur Lecture 6

2. Energy and Pressure Tensor

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2. Energy and Pressure Tensor at V and T

Starting with the integral form of Gibbs' canonical partition function all of thermodynamics follows from differentiation with respect to E and V . The differentiation with respect to V is Tricky , and relies on a change of variable q → (q/L) with the distances scaled by L :

$$Z \propto \prod \int_0^L dq\, e^{-[\mathcal{H}(q,p)/kT]} \propto V^N \prod \int_0^1 d(q/L)\, e^{-[\mathcal{H}(q^*,p)/kT]}$$

$$(\partial \ln Z/\partial \ln V)_T = (P_{xx}V/kT) = N + < \Sigma(xx/r)F/kT > .$$

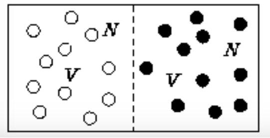
This Virial Theorem makes Pressure measurable in simulations .

Differentiation with respect to T to get Energy is straightforward :

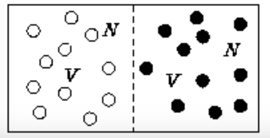
$$(\partial \ln Z/\partial \ln T)_V = (E/kT) = N + < \Phi/kT > . \quad [\text{ in 2D }]$$

Likewise , all of thermodynamics follows from molecular dynamics or from Monte Carlo . This is not to imply that any of the three routes will be "easy" .

3. N! and Gibbs' Paradox



3. N! and Gibbs' Paradox



If we consider two containers of identical fluid separated by a membrane the extensive property of entropy suggests that removing the membrane will not change the entropy, $S_{1+2} = S_1 + S_2$. This property follows from Gibbs' partition function if the particles are treated as "identical". To avoid duplication in the integral the number of states V^N or $(V/2)^N$ is divided by N! or (N/2)! x (N/2)!

$$(N/2)! \times (N/2)! \approx (N/2e)^{(N/2)} \times (N/2e)^{(N/2)} \approx N!/2^N$$

$$(V/2) / (N/2) = (V/N)$$

For identical particles Gibbs' partition functions include the identical-particles correction :

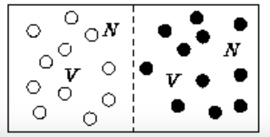
$$\Omega\,(E,V) = e^{[\,S/k\,]} = \#\text{ of E states };$$

$$e^{[\,S/k\,]}\, e^{[\,-E/kT\,]} = e^{[\,-A/kT\,]} \rightarrow$$

$$e^{[\,-A/kT\,]} = (1/N!) \prod \int\!\!\int [\, dqdp/h\,] e^{[\,-\mathcal{H}(q,p)/kT\,]}$$

*** Stirling's Approximation is $N! \approx (2\pi N)^{1/2} e^{(1/12N)+\cdots} \approx (N/e)^N$**

3. N! and Gibbs' Paradox



If we consider two containers of different fluids separated by a membrane (so that the white and the black particles are distinguishable from one another) things are different ! For simplicity we can imagine that the two fluids are ideal gases (argon's isotopes with atomic weights of 36, 38, and 40 are all stable – the other 21 are not) . We can imagine that the two species are "red" and "blue". Removal of the partition when the two gases are different gives an entropy increase of kln2 for every atom as the number of states available to it has suddenly* doubled :

$$\Omega\ (E,V) = e^{[\ S/k\ ]} = \#\text{ of }E\text{ states} \approx (V/e)^N :$$

$$(\ V/2\ )^{N/2}(\ 2\pi mkT\ )^{N/2}/(N/2)!\ (\ V/2\ )^{N/2}(\ 2\pi mkT\ )^{N/2}/(N/2)!$$

becomes

$$(\ V\ )^{N/2}(\ 2\pi mkT\ )^{N/2}/(N/2)!\ (\ V\ )^{N/2}(\ 2\pi mkT\ )^{N/2}/(N/2)!$$

* A local density of red and blue particles could be defined by using smooth-particle weighting functions , with both densities developing as functions of time, an irreversible mixing process .

4. The Mayers' Virial Expansion and van der Waals' Equation of State

4. The Mayers' Virial Expansion and van der Waals' Equation of State

Clausius' Virial Theorem : $< 2K > = - < \sum F \bullet r >$

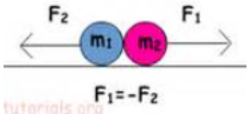
$\sum F \bullet r = \sum ma \bullet r = \sum m(d/dt)(v \bullet r) - \sum mv^2$

Hamonic Oscillator : $< p^2/m > = < \kappa q^2 >$

"Equipartition"

$F_1 \bullet r_1 + F_2 \bullet r_2 = F_{12} \bullet r_{12}$

Positive for repulsions – Negative for attractions



Where F_{12} is the force on 1 due to 2
and where $r_{12} = r_1 - r_2$

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4. The Mayers' Virial Expansion → van der Waals' Equation of State

Three-body example with $Z = (2\pi mkT)^{3/2}Q_3/3!$ and periodic boundaries :

$$Q_3 = \int\int\int \prod (1 + f)dx^3 = \int\int\int[1 + f_{12} + f_{23} + f_{31} + f_{12}f_{23} + f_{23}f_{31} + f_{31}f_{12} + f_{12}f_{23}f_{31}]dx^3$$

$$Q_3 = V^3 + 3(-2V^2) + 3(4V) + (-3V) = V^3 - 6V^2 + 9V = V(V-3)^2$$

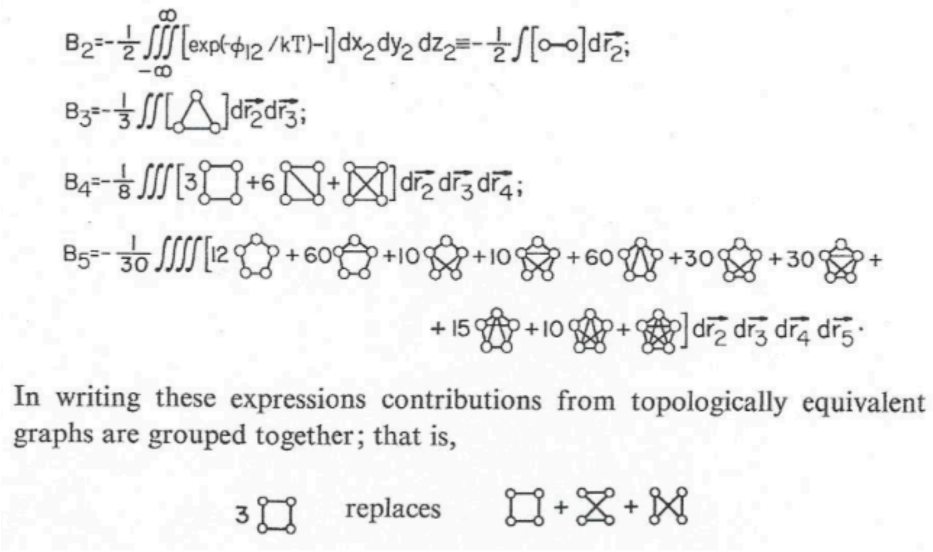
Here f is the Mayers' $f = e^{-\phi/kT} - 1$, with the same range as f .

The clever idea is to convert the Helmholtz free energy into a density series .
The four-particle case involves 64 terms, too much for a single overhead !

How many for 5 ? How many for N ?

4. The Mayers' Virial Expansion for PV/NkT provides accurate fluid properties

$$PV/NkT = 1 + B_2(N/V) + B_3(N/V)^2 + B_4(N/V)^3 + B_5(N/V)^4 + \ldots$$



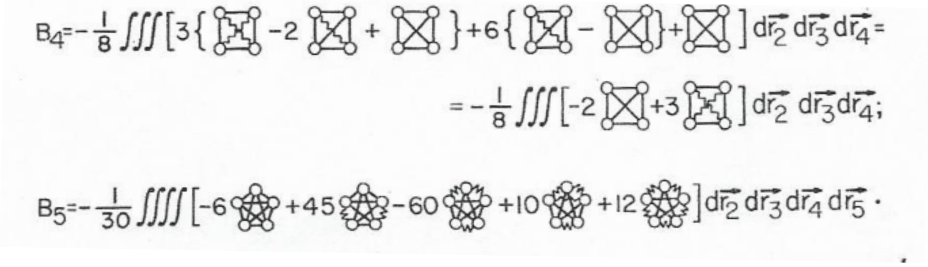
In writing these expressions contributions from topologically equivalent graphs are grouped together; that is,

3 replaces + +

4. Virial Expansion : $PV/NkT = 1 + B_2(N/V) + B_3(N/V)^2 + B_4(N/V)^3 + B_5(N/V)^4 + \ldots$

A particularly simple system is the hard-rod fluid , N particles of unit length in box of length V . The canonical partition function is $(1/N!)\,(V - N)^N(2\pi mkT)^{N/2} \rightarrow PV/NkT = V/(V - N)$ so that each virial coefficient is equal to unity . Carol showed how to calculate the hard-particle integrals contributing to the virial coefficients by Monte Carlo integration .

A profound simplification of the Mayers' formulæ includes Boltzmann-factor bonds (indicated below by wiggly lines) in addition to the Mayers' f bonds , resulting in a tremendous reduction of the computational work. Clisby and McCoy's "Ninth and Tenth Order Virial Coefficients for Hard Spheres in D Dimensions" [arXiv 0503525] was the state of the art in 2005 :



4. Virial Expansion and van der Waals' Equation of State

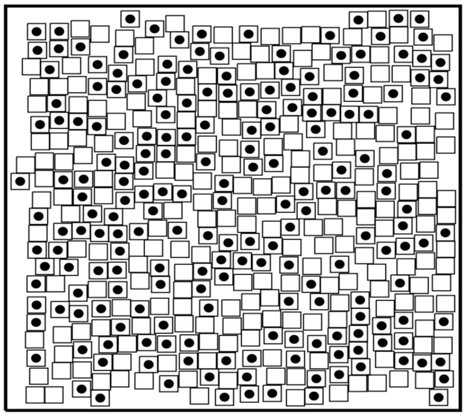
By introducing both $e^{[-\phi/kT]}$ bonds and $e^{[-\phi/kT]} - 1$ bonds Monte Carlo evaluation is greatly simplified

	2	3	4	5	6	7	8	9	10
Mayer	1	1	3	10	56	468	7123	194066	9743542
RH	1	1	2	5	23	171	2606	81564	4980756
RH/Mayer	1	1	0.667	0.500	0.410	0.365	0.366	0.420	0.511
RH, $D=1$	1	1	1	1	1	1	1	1	1
RH, $D=2$	1	1	2	4	15	73	$\gtrsim$647	$\gtrsim$8417	$\gtrsim$110529
RH, $D=3$	1	1	2	5	22	161	>2334	>60902	
RH, $D=4$	1	1	2	5	23	169	>2556	>76318	

← From 2^N to just 1 !

D	B_3/B_2^2	B_4/B_2^3	B_5/B_2^4	B_6/B_2^5	B_7/B_2^6	B_8/B_2^7	B_9/B_2^8	B_{10}/B_2^9
2	0.782004 ···	0.53223180 ···	0.33355604(1)*	0.1988425(42)	0.1148728(43)	0.0649930(34)	0.0362193(35)	0.0199537(80)
3	0.625	0.2869495 ···	0.110252(1)*	0.03888198(91)	0.01302354(91)	0.0041832(11)	0.0013094(13)	0.0004035(15)
4	0.506340 ···	0.15184606 ···	0.0357041(17)	0.0077359(16)	0.0014303(19)	0.0002888(18)	0.0000441(22)	0.0000113(31)
5	0.414063 ···	0.0759724807 ···	0.0129551(13)	0.0009815(14)	0.0004162(19)	−0.0001120(20)	0.0000747(26)	−0.0000492(48)
6	0.340941 ···	0.03336314 ···	0.0075231(11)	−0.0017385(13)	0.0013066(18)	−0.0008950(30)	0.0006673(45)	−0.000525(16)
7	0.282227 ···	0.00986494662 ···	0.0070724(10)	−0.0035121(11)	0.0025386(16)	−0.0019937(28)	0.0016869(41)	−0.001514(14)
8	0.234614 ···	−0.00255768 ···	0.00743092(93)	−0.0045164(11)	0.0034149(15)	−0.0028624(26)	0.0025969(38)	−0.002511(13)

4. Virial Expansion and van der Waals' Equation of State

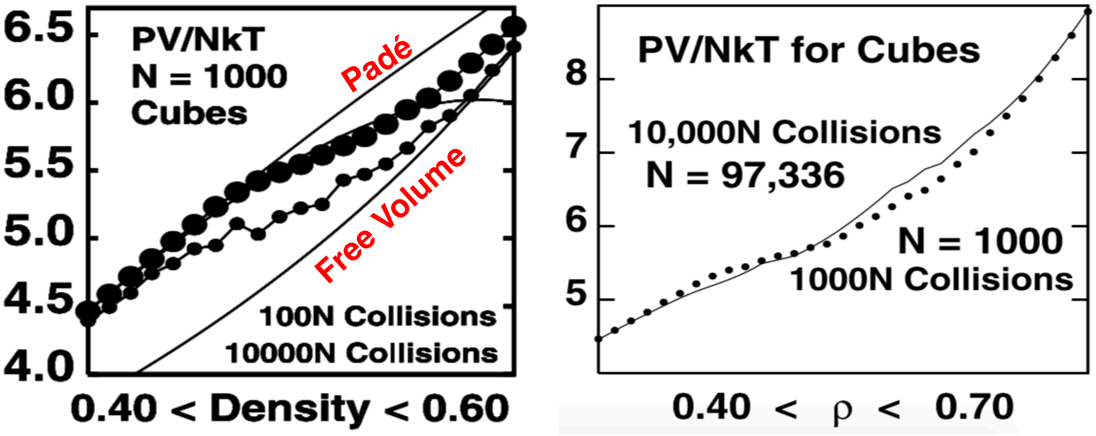


Bob Zwanzig[1] suggested that the virial coefficients for hard spheres could be bounded by considering the cubes fitting just inside and just outside the spheres . This turned out to be wrong .

Despite more numerical work[2] the situation is not yet clear for hard cubes . It would be interesting to see how many of the Ree-Hoover diagrams vanish in the cases of the hard squares and cubes .

1. **R W Zwanzig, "Virial Coefficients of Parallel Square and Parallel Cube Gases", Journal of Chemical Physics 24,** 855-856 **(1956) .**
2. **W G Hoover, A G De Rocco, "Sixth and Seventh Virial Coefficients for the Parallel Hard Cube Model", Journal of Chemical Physics 36,** 3141–3162 **(1962) .**

4. Virial Expansion and van der Waals' Equation of State



"The Region of Confusion for Hard Parallel Cubes" from W G Hoover , C G Hoover , and M N Bannerman, "Single-Speed Dynamics of Hard Parallel Squares and Cubes", [Journal of Statistical Physics 136, 715-732 (2009)]

4. Van der Waals' equation of state and the critical point

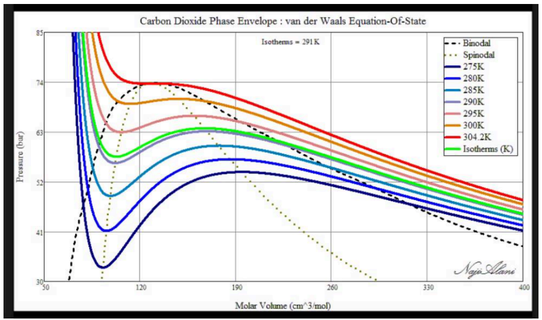
If in addition to a hard repulsion there is a weak attractive potential we can approximate the Canonical partition function by $Z = (V – Nb)^N(2\pi mkT)^N \exp[N^2a/VkT] / N!$ → $PV/NkT = [V/(V – Nb)] – (Na/VkT) = 1 + \rho(b – a/kT) + \rho^2b^2 + \rho^3b^3 + \ldots$

The critical point, above which gas and liquid cannot be distinguished , follows from $(\partial P/\partial\rho) = 0$ with $(\partial^2P/\partial\rho^2) = 0$ → $PV/NkT = 3/8$; rare gases give about 0.30 .

Just using three virial coefficients gives $PV/NkT = 1 + B_2\rho + B_3\rho^2$ from which $1 + 2B_2\rho + 3B_3\rho^2= 0$ and $2B_2 + 6B_3\rho = 0$ → $B_2\rho = – 1$; $B_3\rho^2 = 1/3$ and $PV/NkT = 1/3$

Pressure

CO_2
Isotherms →



The "spinodal" region is unstable in the sense that The fluid's compressibility $– (d\ln V/dP)_T$ is negative .

Volume

5. Partition Function for One-Dimensional Hard Rods of Unit Length

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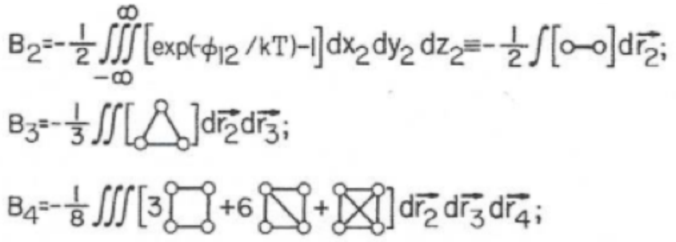


$$B_2 = -\frac{1}{2}\iiint_{-\infty}^{\infty}\left[\exp(-\phi_{12}/kT)-1\right]dx_2\,dy_2\,dz_2 \equiv -\frac{1}{2}\int[\circ\!-\!\circ]\,d\vec{r}_2;$$

$$B_3 = -\frac{1}{3}\iint[\triangle]\,d\vec{r}_2\,d\vec{r}_3;$$

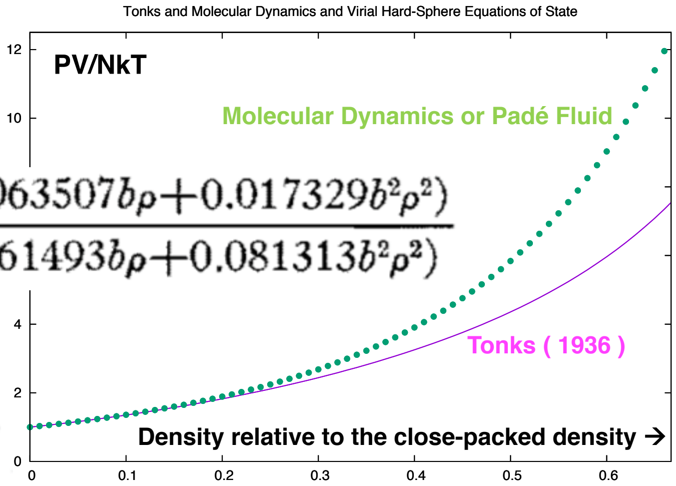
$$B_4 = -\frac{1}{8}\iiint[3\square+6\boxbslash+\boxtimes]\,d\vec{r}_2\,d\vec{r}_3\,d\vec{r}_4;$$

The B_2 integral is – 2 for two rods of unit length with one at the origin → $B_2 = 1$
The B_3 integral is – 3 for three rods with one at the origin → $B_3 = 1$
The B_4 integrals are 3(16/3) – 6(14/3) + 1(12/3) = – 8 → $B_4 = 1$ [all the $B_N = 1$]

This Tonks' Gas problem is a good introduction to Monte Carlo integration . See also "The Complete Equation of State of One , Two , and Three-Dimensional Gases of Hard Elastic Spheres" by Lewi Tonks in Physical Review 50 , 955-963 **(1936) .**

5. One-Dimensional Hard Rods Generalized as of 1936

Tonks' idea in two or three dimensions was to reproduce the third virial coefficient and to guarantee that the pressure diverged at close packing . Let's see how close he came, in 1936, to the truth for hard spheres , which came about twenty years later .



Padé :

$$\frac{V}{N}\left[\frac{PV}{NkT}-1\right] \equiv \frac{b(1+0.063507b\rho+0.017329b^2\rho^2)}{(1-0.561493b\rho+0.081313b^2\rho^2)}$$

Tonks :

$$pv = NkT\frac{1+2.9619\theta+5.4830\theta^2}{1-0.8517\theta^3-0.1483\theta^4}.$$

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6. Gibbs' Canonical Partition Function for the Harmonic Chain

6. Gibbs' Canonical Partition Function for the Harmonic Chain

A chain of N+1 harmonic oscillators joined by N nearest-neighbor springs with the first oscillator fixed at the origin provides a partition function that is a simple Gaussian integral . We can work it out for three springs from which the general case is clear :

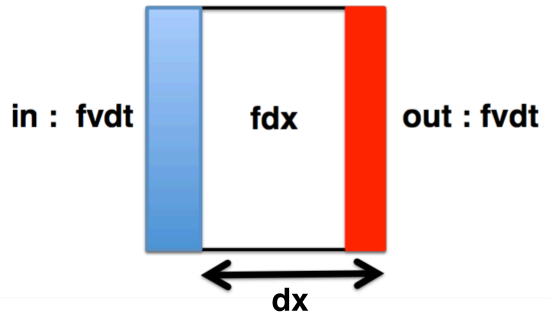
$\iint \exp[-\kappa(q_1-q_2)^2/2kT-\kappa(q_2-q_3)^2/2kT\,]dq_2dq_3=(2\pi kT/\kappa)^{1/2}\int \exp[-\kappa(q_1-q_2)^2/2kT\,]dq=(2\pi kT/\kappa)^{N/2}$

There is a general expression giving Gaussian integrals of a symmetric matrix $\kappa_{ij}x_ix_j$ in terms of the determinant of κ . This makes it possible to work out partition functions in many dimensions for crystals with defects such as holes or surfaces . Normal modes of vibration , free energies , and mean squared displacements can be found by solving the eigenvalue problem presented by the "dynamical matrix" κ or A (below) .

$$\int_{-\infty}^{\infty} e^{\left(-\frac{1}{2}\sum_{i,j=1}^{n} A_{ij}x_ix_j\right)}\, d^n x = \int_{-\infty}^{\infty} e^{\left(-\frac{1}{2}x^T A x\right)}\, d^n x = \sqrt{\frac{(2\pi)^n}{\det A}}$$

7-8. Nonequilibrium Fluid Mechanics generalizes Thermodynamics to include *nonequilibrium* flows of momentum and energy

To what extent is the Continuity Equation Obvious ?

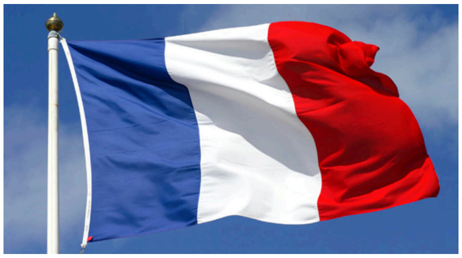


in : fvdt

fdx

out : fvdt

dx



The Flag of France

An important observation :
During the short time dt the flow into the fixed Eulerian bin is fvdt from the left with a loss – fvdt on the right. Evidently the change in fdx during dt becomes $-\partial(fv/\partial x)dtdx$ So that the conservation law in one dimension is $(\partial f/\partial t) = -\partial(fv)/\partial x$. There is nothing To stop us from summing up contributions in the x and y and z directions if desired, or even in *all* the phase-space directions if we would like to prove Liouville's Theorem .

7-8. The Continuity Equation , or the "Control Volume" Approach , gives Eulerian and Lagrangian Versions of the Continuum Equations

$$d\rho/dt \equiv \partial\rho/\partial t + v\cdot\nabla\rho = -\rho\nabla\cdot v \; ; \quad \text{(Reversible)}$$

$$\rho dv/dt \equiv \rho\partial v/\partial t + \rho v\cdot\nabla v = -\nabla\cdot P \; ;$$

$$\rho de/dt \equiv \rho\partial e/\partial t + \rho v\cdot\nabla e = -P:\nabla v - \nabla\cdot Q \; .$$

The derivations are simplest in one space dimension where the change in Mass, Momentum, or Energy is given by the flows into and out of a control volume of length dx . It is essential to recognize that the flow of comoving momentum is given by the pressure tensor and that the flow of comoving energy is given by the heat flux vector (these two are P and Q) . See the derivations in *Molecular Dynamics* + *Computational Statistical Mechanics* .

7-8. Nonequilibrium Fluid Mechanics generalizes Thermodynamics to include *nonequilibrium* flows of momentum and energy

The pressure tensor P is the comoving momentum flux . Let us imagine averaging the momentum flux in a zone containing many particles . With pair forces a y line sampling momentum flux has a probability $| y_{ij} | / L_y$ of intercepting the flow of momentum F_y between particles i and j .

There is an addition a convective flow, in which a particle moving with momentum p_y has a contribution to the flux proportional to pp_y/m .

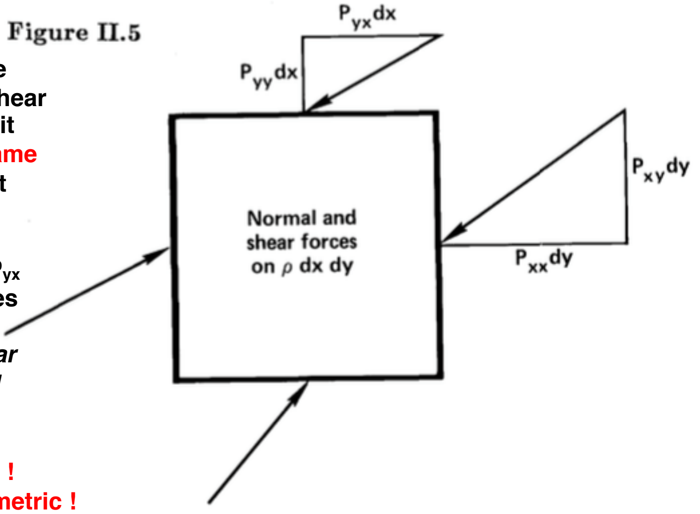
Adding the action-at-a-distance and convective contributions gives

$P_{xx}V = \Sigma p_x p_x/m - \Sigma xxF/r$ **and** $P_{xy}V = P_{yx}V = \Sigma p_x p_y/m - \Sigma xyF/r$

These same results are obtained if one takes the equation of motion , multiplies by x or y , and time averages , including wall forces . That was the method we used earlier to get Clausius' Virial Theorem .

7-8. Nonequilibrium Fluid Mechanics generalizes Thermodynamics to include the *nonequilibrium* flux of momentum (pressure tensor)

Figure II.5



The two-dimensional Cartesian volume element shown here has normal and shear forces on each face . The force per unit length defines the pressure tensor (same as minus the stress tensor) in the limit that the element is small .

In that same limit it is necessary that P_{yx} and P_{xy} are equal . Otherwise the forces lead to infinite angular acceleration in this limit . For the details see *Molecular Dynamics* or *Computational Statistical Mechanics* .

Force ≈ dx and mass ≈ dxdy → Trouble !
The Pressure Tensor is therefore symmetric !

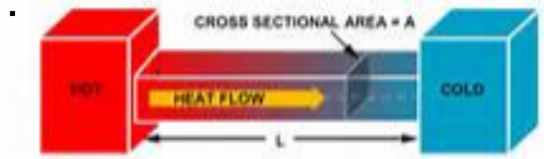
8. Two derivations of the nonequilibrium heat flux vector Q for pair forces

A first approach considers the changing energy of interacting particles :

$$de_1 /dt = F_{12}\cdot (v_1 + v_2)/2 = de_2 /dt \quad *$$

Here F_{12} is the force on particle 1 due to its interaction with particle 2 . Thus there is an "action-at-a-distance" contribution $[x_{12} F_{12} \cdot < v >]$ to the flux in the x direction in addition to the convective contributions $e_1v_1 + e_2v_2$ in the directions of the particle motions .

In molecular dynamics simulations we can maintain temperatures of selected degrees of freedom by using Gauss' or Nosé-Hoover forces . Keeping track of the heat extracted or inserted by these forces is an alternative method for measuring the flux .



* Each particle has $(1/2)\phi_{12}$.

8. Two derivations of the nonequilibrium heat flux vector Q for pair forces

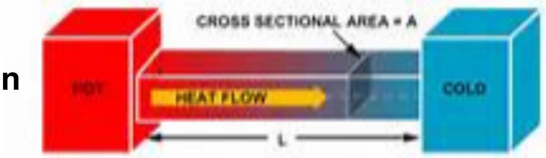
A different approach, like Clausius', takes the equation for (de_i/dt) and multiplies by r_i . We will simplify to one dimension and include only a single pair force to keep the notation simple :

$$< x(de/dt) = (d/dt)(xe) - e(dx/dt) = x[mv(dv/dt) - (1/2)F< v >] = LQ_x >$$

The brackets < . . . > indicate a time average , which makes it possible to delete the term in black (the time derivative of a bounded quantity has eventually to vanish) . It is a good homework problem to expand this sketch to agree with the heat flux vector derived on page 59 of *Molecular Dynamics* (where the components of Q and r match) :

$$QV = \sum(pe/m) + \sum\sum r [F \bullet (p_i+p_j)/(2m)]$$

It is "no problem" to extend this derivation to mixtures with manybody forces .



9. Stress in systems with gravitational and rotational contributions .

Motivation for this work came from the configurational temperature :

$$\langle \nabla^2 \mathcal{H} \rangle = \langle (\nabla \mathcal{H})^2 \rangle / kT \rightarrow kT_C \equiv \langle (\nabla \mathcal{H})^2 \rangle / \langle \nabla^2 \mathcal{H} \rangle .$$

---

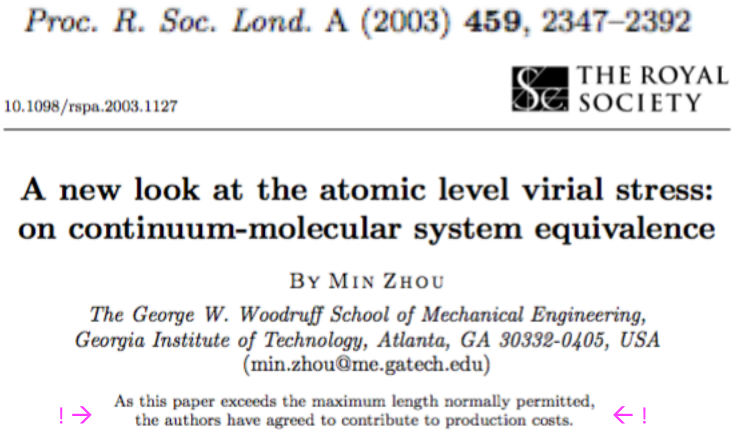
9. Stress in systems with gravitational* and rotational contributions .

There is an extensive literature relating the atomistic pressure tensor , formulated by Irving and Kirkwood (JCP 1950) in terms of delta functions, to the continuum stress tensor ($\sigma = -P$) . To shed light on the subject we study two problems with gravitational and rotational contributions to the stress . Notice that a constant gravitational field has a vanishing second derivative, $(d/dy)^2(mgy) = 0$, so that a straightforward implementation of configurational temperature * gives infinity !

For some reason there is an extensive literature composed of efforts to make contact between the Irving-Kirkwood formalism (atomistic , with delta functions) and traditional continuum mechanics (continuous differentiable field functions) . Because the two approaches differ in their underlying concepts there is no exact link . Resolutions of the difference are arbitrary so that picking the "best" one is subjective .

$$^{*}\langle \nabla^2 \mathcal{H} \rangle = \langle (\nabla \mathcal{H})^2 \rangle / kT \rightarrow kT_C \equiv \langle (\nabla \mathcal{H})^2 \rangle / \langle \nabla^2 \mathcal{H} \rangle .$$

9. Stress in systems with gravitational and rotational contributions .



Proc. R. Soc. Lond. A (2003) **459**, 2347–2392

10.1098/rspa.2003.1127

THE ROYAL SOCIETY

A new look at the atomic level virial stress: on continuum-molecular system equivalence

BY MIN ZHOU

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! → As this paper exceeds the maximum length normally permitted, the authors have agreed to contribute to production costs. ← !

From the abstract: "The conceptual flaw in the generalization from the virial theorem for gas pressure to stress and the confusion over spatial and material equations of balance of momentum in theoretical derivations of the virial stress that led to its erroneous acceptance as the Cauchy stress are pointed out ."

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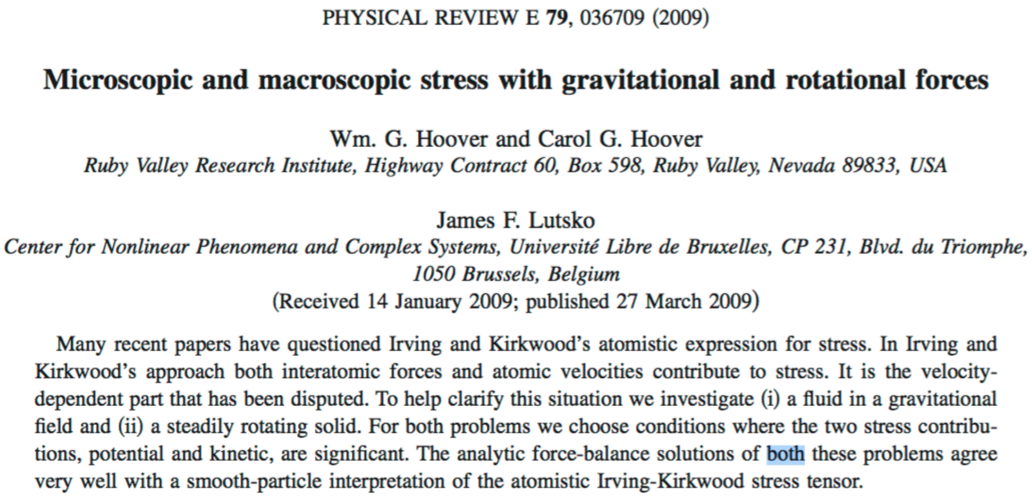
9. Stress in systems with gravitational and rotational contributions .



PHYSICAL REVIEW E **79**, 036709 (2009)

Microscopic and macroscopic stress with gravitational and rotational forces

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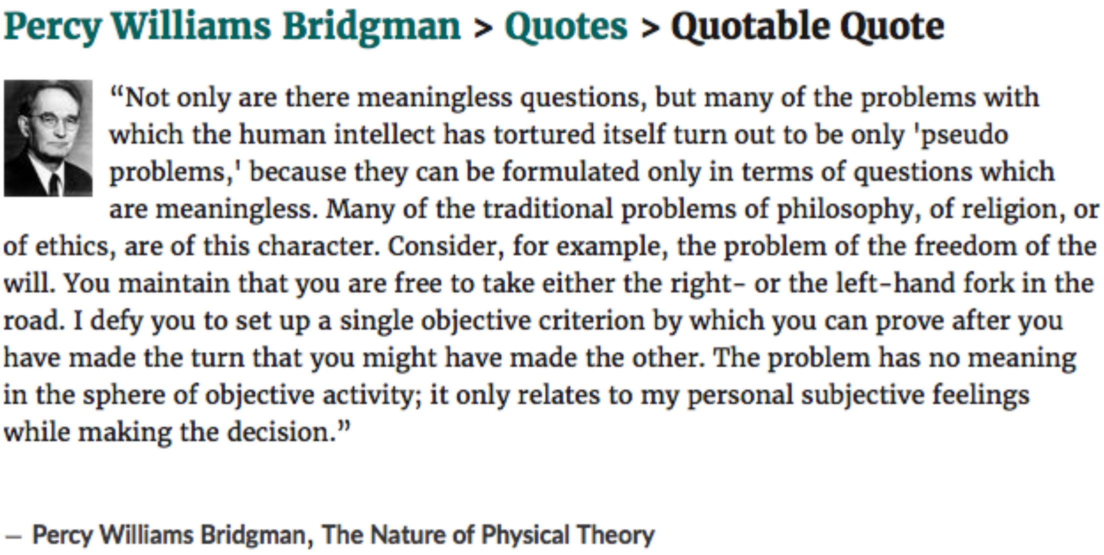
(Received 14 January 2009; published 27 March 2009)

Many recent papers have questioned Irving and Kirkwood's atomistic expression for stress. In Irving and Kirkwood's approach both interatomic forces and atomic velocities contribute to stress. It is the velocity-dependent part that has been disputed. To help clarify this situation we investigate (i) a fluid in a gravitational field and (ii) a steadily rotating solid. For both problems we choose conditions where the two stress contributions, potential and kinetic, are significant. The analytic force-balance solutions of both these problems agree very well with a smooth-particle interpretation of the atomistic Irving-Kirkwood stress tensor.



Percy Williams Bridgman > Quotes > Quotable Quote

“Not only are there meaningless questions, but many of the problems with which the human intellect has tortured itself turn out to be only 'pseudo problems,' because they can be formulated only in terms of questions which are meaningless. Many of the traditional problems of philosophy, of religion, or of ethics, are of this character. Consider, for example, the problem of the freedom of the will. You maintain that you are free to take either the right- or the left-hand fork in the road. I defy you to set up a single objective criterion by which you can prove after you have made the turn that you might have made the other. The problem has no meaning in the sphere of objective activity; it only relates to my personal subjective feelings while making the decision.”

― Percy Williams Bridgman, The Nature of Physical Theory

This point of view simplifies life considerably. Bridgman was a fan of operationalism .

---

9. Stress in systems with gravitational* and rotational contributions .

Both kinetic and potential contributions to the pressure are important in this problem where the pair potential is a short-ranged repulsion with an integral (using $2\pi r dr$) of unity :

$$\phi_{Cusp}(r < h) = (10/\pi h^2)[\,1 - (r/h)\,]^3$$

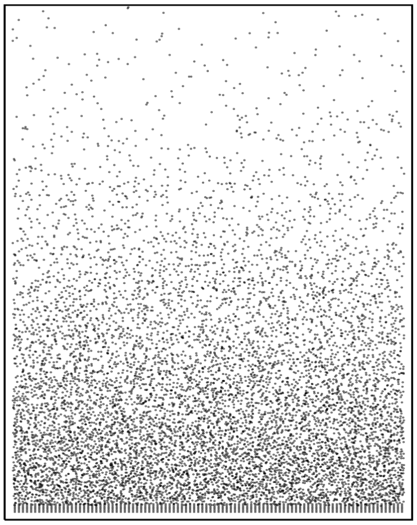
Evidently the potential energy of a particle is half its density .
The contribution of the interparticle forces to PV follows from an integration by parts :

$$(1/2)\Sigma F\bullet r = (N/4) < -\phi' r > = (N/2) < \phi > = (N/2)\,\rho \rightarrow P = \rho^2/2 \,.$$

The simulation is isothermal (kT = 1) . We calculate the local density and temperature $< p^2/2 >$ as Lucy-function averages :

$$w(\,r < 3\,) = (5/9\pi)(\,1 - 6x^2 + 8x^3 - 3x^4\,) \text{ where } x = r/h = r/3 \,.$$

There are 9216 gas particles supported by 6•96 = 576 fixed particles at the bottom . The gravitational field is chosen so that the maximum density matches the density at bottom , 2 .



-50 < x < +50

*** Hoovers and Lutsko arXiv 0901.2071**

9. Stress in systems with gravitational and rotational contributions .

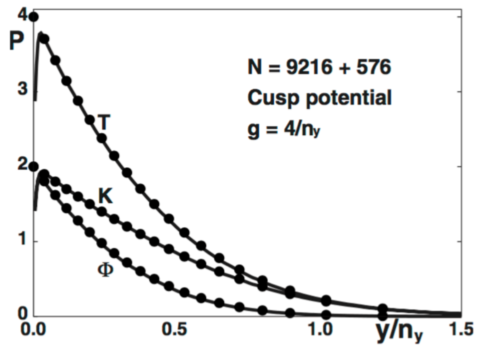


FIG. 2. Comparison of the observed and analytic pressure profiles for the gravitational problem shown in Fig. 1. From top to bottom the three curves are the total (T or Irving-Kirkwood), kinetic (K), and potential (Φ or Zhou) contributions to the pressure profile. These observed pressure contributions are calculated as smooth-particle averages. The points correspond to the analytic expressions from the isothermal equation of state $P_T=P_\Phi+P_K=(\rho^2/2)+\rho$.

Equation of State :

$P = (\rho^2/2) + \rho T = (\rho^2/2) + \rho$

Force Balance :

$dP/dy = (dP/d\rho)(d\rho/dy) = -\rho g$

$(\rho+1)(d\rho/dy) = -\rho g \rightarrow$

Integrate dρ and dy :

$\int (\rho+1) d\ln\rho = \int -g\,dy$

With the result * :

$\rho - 2 + \ln(\rho/2) = -gy$

Gravitational Force :

$P(y) = g \int_y^\infty \rho(y)dy$

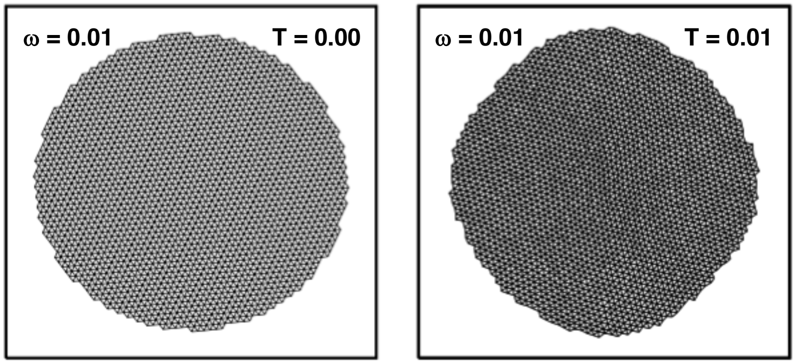
*** Now What ?**

9. Stress in systems with gravitational and rotational contributions .

From the gravitational problem we see that the continuum force balance between pressure and gravity is reproduced perfectly everywhere other than at the base where the boundary condition for the atomistic situation is not faithful to the continuum problem . This slight variation on the barometer problem confirms that the atomistic formulation of stress is in excellent consonance with the continuum formulation .

Next we address rotational contributions to mechanical equilibrium . Again we will find that the kinetic and potential contributions to the stress can be similar in magnitude . Both are necessary to a proper mechanical equilibrium .

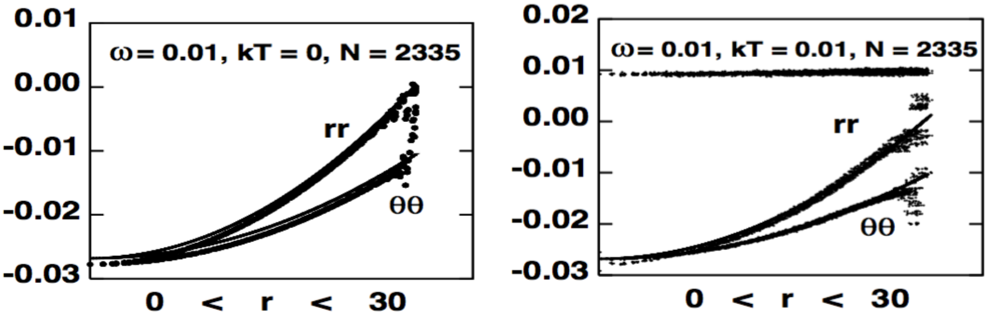
9. Stress in systems with gravitational and rotational contributions .



2335 particles with 6828 Hooke's-Law nearest-neighbor bonds . The cold crystal shows straight rows . The initial structure is taken from a perfect triangular lattice including all the particles within a maximum distance of √637 = 25.239 . The force balance for the rotating crystal requires both kinetic and potential contributions in order to match the continuum stress calculation from linear elastic theory .

9. Stress in systems with rotational contributions .

The equilibration phase involved thermostating the radial momenta while rescaling the angular momenta to generate thermally-equilibrated steadily-rotating solid disks . Ten equally-spaced rotation rates were studied . The figures show the molecular dynamics cold and hot data as points and the predictions of linear elastic theory as lines . The outer boundary is poorly described by discrete points but the interior stress fields are in good agreement with the predictions of linear elastic theory . The thermal part of PV is +0.01 in the right panel and 0.00 in the cold-crystal left panel .



9. Stress in systems with rotational contributions* .

The linear elastic theory for a rotating disk requires the Lamé constants * and a solution of the force-balance between the centrifugal and tensile stresses :

$$0 = +\rho\omega^2 r + (\partial\sigma_{rr}/\partial r) + (\sigma_{rr} - \sigma_{\theta\theta})/r \ .$$

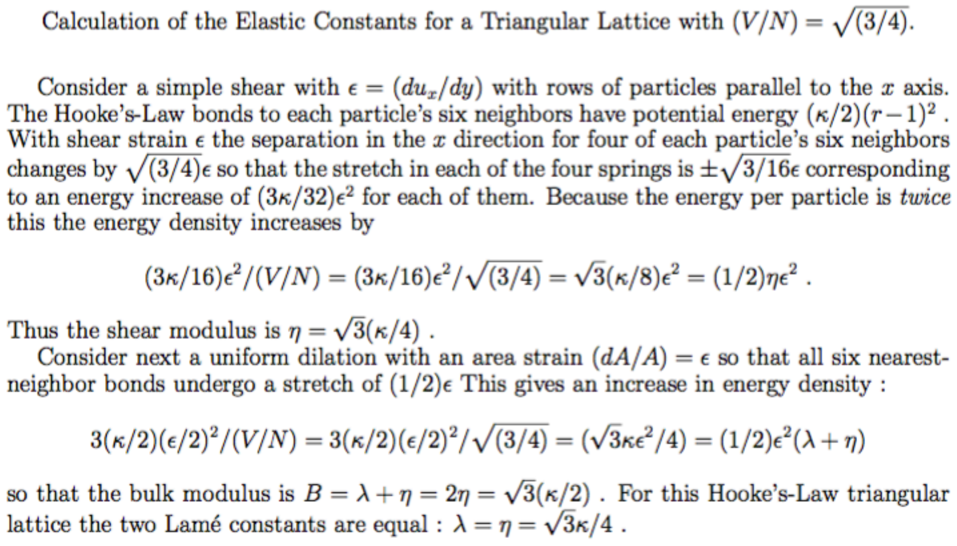
The solution which has a vanishing radial stress at the outer radius R is :

$$\sigma_{rr} = (\rho\omega^2/12)[5R^2 - 5r^2] \ ; \ \sigma_{\theta\theta} = (\rho\omega^2/12)[5R^2 - 3r^2] \ .$$

The preceding graphic showed that both stress tensor components agree nicely with the results of molecular dynamics in which the potential and kinetic stress contributions are both of the same order of magnitude as the rotational effects .

* $\sigma = \left[\sigma_{eq} + \lambda\nabla\cdot u\right] I + \eta\left[\nabla u + \nabla u^{transpose}\right]$ **with** $\lambda = \eta = \sqrt{3/16}$

Useful Exercise : Finding the Lamé Constants in a Hooke's-Law Crystal



Calculation of the Elastic Constants for a Triangular Lattice with $(V/N) = \sqrt{(3/4)}$.

Consider a simple shear with $\epsilon = (du_x/dy)$ with rows of particles parallel to the x axis. The Hooke's-Law bonds to each particle's six neighbors have potential energy $(\kappa/2)(r-1)^2$. With shear strain ϵ the separation in the x direction for four of each particle's six neighbors changes by $\sqrt{(3/4)}\epsilon$ so that the stretch in each of the four springs is $\pm\sqrt{3/16}\epsilon$ corresponding to an energy increase of $(3\kappa/32)\epsilon^2$ for each of them. Because the energy per particle is *twice* this the energy density increases by

$$(3\kappa/16)\epsilon^2/(V/N) = (3\kappa/16)\epsilon^2/\sqrt{(3/4)} = \sqrt{3}(\kappa/8)\epsilon^2 = (1/2)\eta\epsilon^2 \ .$$

Thus the shear modulus is $\eta = \sqrt{3}(\kappa/4)$.

Consider next a uniform dilation with an area strain $(dA/A) = \epsilon$ so that all six nearest-neighbor bonds undergo a stretch of $(1/2)\epsilon$ This gives an increase in energy density :

$$3(\kappa/2)(\epsilon/2)^2/(V/N) = 3(\kappa/2)(\epsilon/2)^2/\sqrt{(3/4)} = (\sqrt{3}\kappa\epsilon^2/4) = (1/2)\epsilon^2(\lambda+\eta)$$

so that the bulk modulus is $B = \lambda + \eta = 2\eta = \sqrt{3}(\kappa/2)$. For this Hooke's-Law triangular lattice the two Lamé constants are equal : $\lambda = \eta = \sqrt{3}\kappa/4$.

10. Levesque-Verlet Bit-Reversibility

10. Levesque-Verlet Bit-Reversibility

```
do 30 it = 1,itmax
idtdtF = dt*dt*(-iqnow)
iqnew = 2*iqnow - iqold + idtdtF
iqnow = iqnew
iqold = iqnow
iqnow = iqnew
write(6,*) it,iqnow
30 continue
```

It is remarkable that using this trick (integer arithmetic for the forces and the coordinates) allows the motion to be reversed precisely , to the very last bit ! It is convenient to choose dt equal to unity so that the forces and the coordinates are similar in size .

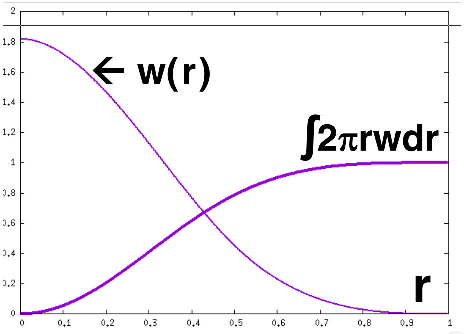
Problems which obey the Second Law of Thermodynamics when generated can be reversed to the very last bit , generating a flow that contradicts the Second Law . Using integers is very much like recording pixels of a movie frame and playing the movie in the backward direction . So long as the equations of motion are Hamiltonian there is no contradiction with classical mechanics .

10. Levesque-Verlet Bit-Reversibility with Smooth-Particle Continuum Mechanics *

Simple equation of state with compressibility and thermal expansion :

$$P = -\sigma = \rho^2 - 1 - e$$

There is a stable leapfrog algorithm solution using :



$$w(0 < r < 1/2) = (40/7\pi)(1 - 6r^2 + 6r^3)$$

$$w(1/2 < r < 1) = (80/7\pi)(1 - r)^3$$

[Monaghan’s weight function]

* **Kum and Hoover, Journal of Statistical Physics 76** , 1075 -1081 **(1994) .**

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10. Levesque-Verlet Bit-Reversibility with Smooth-Particle Continuum Mechanics *

Simple equation of state with compressibility and thermal expansion :

$$P = -\sigma = \rho^2 - 1 - e$$

There is a stable leapfrog algorithm solution using :

$$r_+ - 2r_0 + r_- \equiv dt^2 \sum ([(m\sigma/\rho^2)_i + (m\sigma/\rho^2)_j] \cdot \nabla_i w_{ij})_0$$

$$e_+ - e_- \equiv -dt \sum [(m\sigma/\rho^2)_i + (m\sigma/\rho^2)_j]_0 : v_{ij}(\nabla_i w_{ij})_0$$

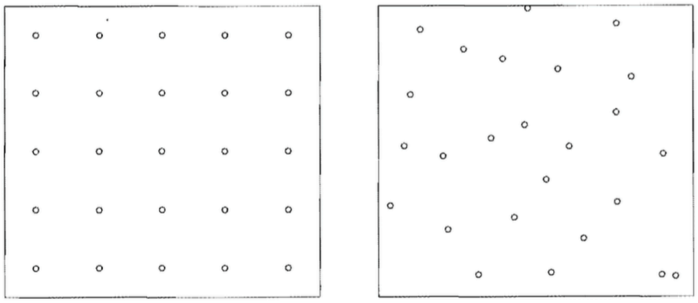
$$2dtv_{ij} \equiv (r_+ - r_-)_i - (r_+ - r_-)_j$$

Notice the lack of any dissipation . There is no viscosity and no heat conductivity . The algorithm is stable for timesteps of 0.01 and 0.02 with kinetic and interal energies of 1 per particle and 25 particles In a 2.5 x 2.5 box. The time-averaged energy values are E = 33.94 and K = 16.05 .

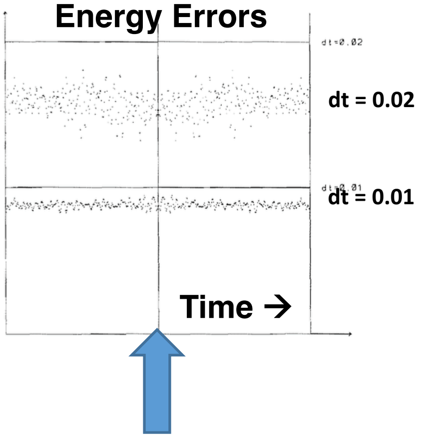
* **Kum and Hoover, Journal of Statistical Physics 76 , 1075-1081 (1994) .**

10. Levesque-Verlet Bit-Reversibility with Smooth-Particle Continuum Mechanics *

Initial = Final Coordinates and Coordinates at Time Reversal Time



Energy Errors



Time-Reversal at Time = 10

$$P = -\sigma = \rho^2 - 1 - e$$

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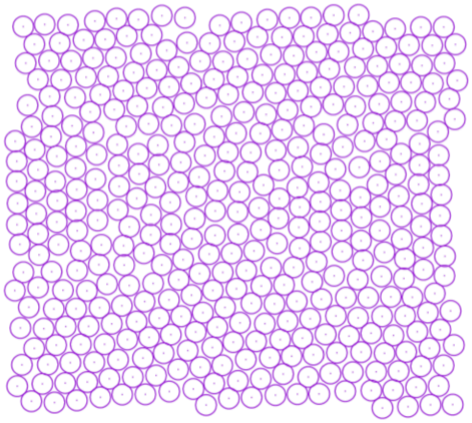
10. Levesque-Verlet Bit-Reversibility with Smooth-Particle Continuum Mechanics *



Because the weight function is smooth and includes a few dozen particles typical morphologies are fluid . By choosing a weight function range of 1 and simple Isentropic equations of state [$de = -Pdv = (P/\rho^2)d\rho$] ,

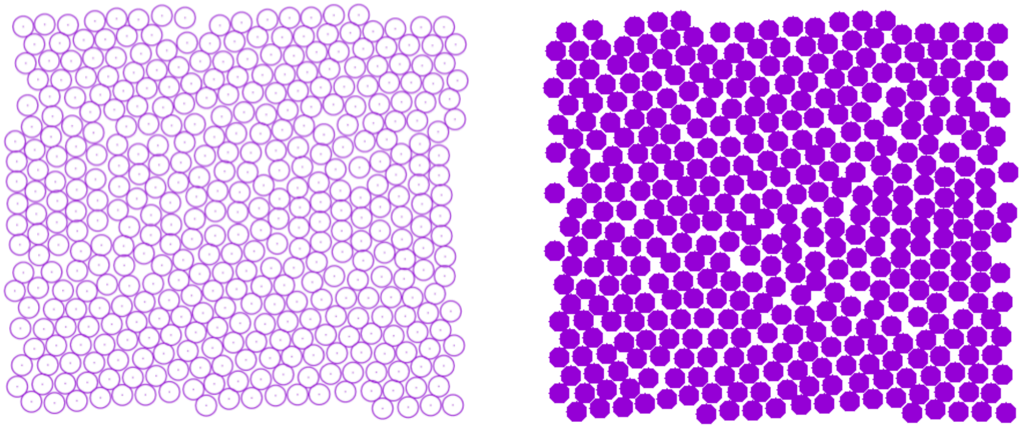
$$P = (\rho^3 - \rho^2) \leftarrow \text{or} \rightarrow P = (1/2)(\rho^{-1} - \rho^{-2}) ,$$

it is possible to obtain reasonable solids with the close-packed triangular lattice structure . This one started out as a 20 x 20 square lattice with very little kinetic energy and ended up in a triangular lattice with just a few defects . h = 1 and constant energy .

Such models should provide a good start to some interesting research questions .

* $P = (\rho - 1)/\rho^2$

10. Levesque-Verlet Bit-Reversibility with Smooth-Particle Continuum Mechanics *



These started off with identical structure and velocities, but with two different equations of state and h = 1 .

* $P = (\rho - 1)\rho^2$

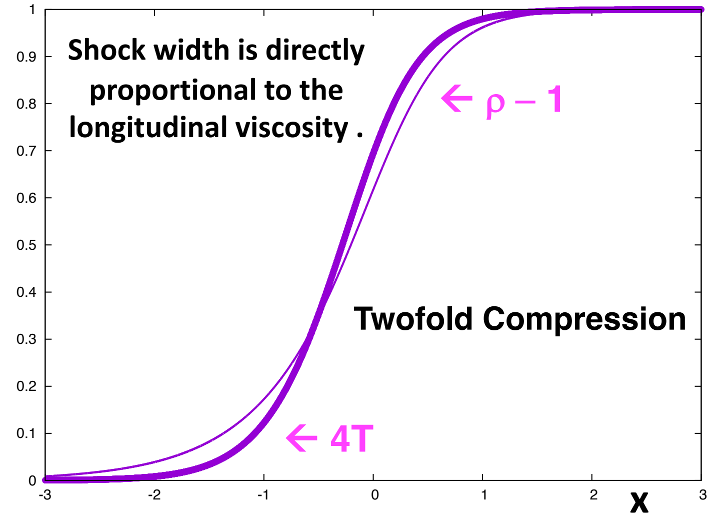
11. Stationary Shockwaves amd Free Expansion

11. Stationary Shockwave Structure with Unit Viscosity *

$P_{xx} = P - \lambda(du/dx + dv/dy) - 2\eta(du/dx)$;
$P_{yy} = P - \lambda(du/dx + dv/dy) - 2\eta(dv/dy)$.

ρu , $P_{xx} + \rho u^2$, and $\rho u[e + (u^2/2) + (P_{xx}/\rho)]$, The fluxes of mass , momentum, and energy , are constant throughout .

Elimination of the cold and hot speeds gives the Hugoniot relation :
$\Delta e = < P > \Delta V$.



Shock width is directly proportional to the longitudinal viscosity .

Twofold Compression

* η and λ are the first and second viscosity coefficients, with η the “shear viscosity” .

---

11. Shockwave and Free-Expansion (isentropic) Curves Fluxes of Mass, Momentum, and Energy

Stationary states are the simplest to analyze . In a one-dimensional shockwave we can examine a differential “control volume” and note that the mass entering and the mass leaving are identical , ρu , where ρ is the mass density and u is the velocity . We choose the systematic flow parallel to the x axis .

The x momentum entering and leaving our control volume are likewise identical and equal to the momentum flux $P_{xx} + \rho u^2$ (per unit area and time) . The change in energy is relatively complicated . It includes the work done by the pressure forces at the boundaries of our volume , $P_{xx} u$. The complete energy flux is the sum of the four contributions : $Q_x + \rho u[e + (u^2/2) + (P_{xx}/\rho)]$.

If we choose an equation of state $P = \rho e = (\rho^2/2) + \rho T$ with $e = (P/\rho) = (\rho/2) + T$, we can identify the fluxes and equilibrium end conditions for a stationary shock :

$u : 2 \rightarrow 1$; $\rho : 1 \rightarrow 2$; $P : (1/2) \rightarrow (5/2)$; $e : (1/2) \rightarrow (5/4)$; $T : 0 \rightarrow (1/4)$

Constant fluxes : $\rho u = 2$; $P_{xx} + \rho u^2 = (9/2)$; $\rho u[e + (P_{xx}/\rho) + (u^2/2)] = 6$.

We have assumed $P = (\rho^2/2) + \rho T - (du/dx)$ and $Q = 0 \rightarrow (d\rho/dx) = (3\rho/2)(\rho - 1)(2 - \rho)$

This single ordinary differential equation can be solved with our RK4 integrator .

11. Continuation of the stationary shockwave problem

We have assumed viscosity * $\eta = -\lambda = 1$ with no thermal conductivity giving

$$P_{xx} = \rho e - \eta (du/dx) = (\rho^2/2) + \rho T - (du/dx) \text{ and } Q = 0$$

$$\rightarrow (d\rho/dx) = (3\rho/2)(\rho - 1)(2 - \rho) \ .$$

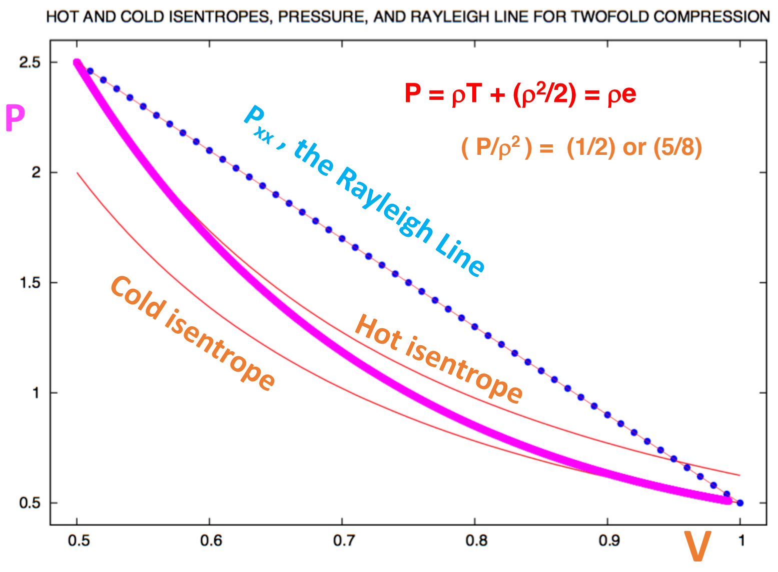
This single ordinary differential equation with a positive righthand side for $1 < \rho < 2$ can be solved using RK4 . Heat flux could be included, resulting in two equations rather than one . It is noteworthy that P_{xx} varies linearly with volume and that *the viscosity determines the width of the shock* . The partition function can be evaluated from e and P :

$$Z = VTe^{(-\rho/2T)} \rightarrow P = \rho T + (\rho^2/2) = \rho e \text{ with } e = T + (\rho/2T) \ ; \ S = \ln(T/\rho)$$

so that the original entropy is $-\infty$. An isentrope results if $T \ \alpha \ \rho$ and $P \ \alpha \ \rho^2$. Let's have a look at P_{xx} , P , and the hot and cold isentropes nearby →

* The "bulk" viscosity is $\eta + \lambda$; setting it equal to zero is "Stokes' approximation" .

11. Continuation of the stationary shockwave problem



11. Shockwaves , Free Expansion , Joule-Thomson Experiment

The usual explanation of a shockwave's singular nature is to state that the denser portion of the wave catches up . If $P = \rho^2/2$ then $c^2 = (\partial P/\partial \rho)_S = \rho$. In the case of free expansion the enthalpy E + PV is converted into kinetic energy, $v^2/2$ with the velocity greater than the sound speed $v = \sqrt{2}\, c$. Note that the sound velocity in the comoving frame is continually decreasing in that it is proportional to the local density .

As the wave spreads out the velocity gradient approaches zero and the free expansion is isentropic . Evidently free expansion is a way to determine the isentropic equation of state .

In the Joule-Thomson experiment the velocity is ignored so that energy balance just gives the information that the enthalpy E + PV is conserved . If the potential energy decreases the comoving temperature (relative kinetic energy) increases and *vice versa* . All of these one-dimensional flows are related to enthalpy .

A Useful Exercise : Relating Sound Velocity to the Bulk Modulus

Calculation of the Sound Velocity c from the Adiabatic Bulk Modulus B

Define displacement $u(x,t)$ in a rightward traveling sound wave with wave vector k , frequency ω , and sound velocity $c = (\omega/k)$ as follows :

$$u = \sin(kx - \omega t) \ ; \ k \equiv (2\pi/\lambda) \ ; \ \omega \equiv 2\pi\nu \ .$$

Substitution of this traveling wave into the equation of motion relates the sound velocity to the (adiabatic) bulk modulus B :

$$\rho\ddot{u} = -\nabla P = B\nabla^2 u \longrightarrow -\rho\omega^2 u = -Bk^2 u \longrightarrow c = (\omega/k) = \sqrt{(B/\rho)} \ .$$

Summary of Lecture 6 :

Gibbs' partition function provides e and P with mechanical fluxes providing P and Q even far from equilibrium. The virial series provides equation of state information which is useful for gases . The use of weight functions makes it possible to generate fields from point data with stress and strains consistent with the predictions of linear elasticity . Shockwaves, isentropes, and adiabatic flows provide good exercises in computational fluid dynamics . Levesque and Verlet's bit-reversible algorithm allows for the analysis of nonequilibrium flows in either time direction .

Addendum : Entropy Production

Extending thermodynamics to nonequilibrium situations requires constitutive relations giving the stress and heat flux in terms of gradients . The Boltzmann equation furnishes a guide . Here we will consider shear flow and heat flow as examples . In periodic shear the temperature can be stabilized by Nosé-Hoover control to reach a steady state. In the steady state heat is extracted by forces { $-\zeta$ p } and work is performed by the shearing boundary conditions $P_{xy}V(du_x/dy)$ with these energy sinks and sources balancing for long time averages , $\langle dE/dt \rangle = \langle dQ/dt \rangle - \langle dW/dt \rangle$. What is the "entropy" of the sheared fluid ? By adding the extracted heat divided by the thermostat temperature T one finds that the entropy decreases at the rate $-\Sigma\, \zeta p^2 /T = -\, 2N \langle \zeta \rangle$. But of course in a steady state there can be no steady decline – entropy (if it exists) must be constant . The result of this line of thinking is entropy production, $dS/dt = -\,(1/T)dQ/dt - P_{xy}V(du_x/dy)/T$. If the viscosity is defined by $P_{xy} = -\eta\,(du_x/dy)$ then the entropy production per unit volume can be expressed as the square of the stress divided by viscosity or the square of the strain rate multiplied by the viscosity, in either case dividing by the thermostat temperature T .

Addendum : Entropy Production

A similar idea can be applied to heat flow . The heat extracted by the cold reservoir gives an entropy loss Q/T while the heat added by the hot reservoir provides an entropy gain . Because there is no long time change in system energy the entropy change is $< Q >[1/T_H – 1/T_c] < 0$. If the temperature difference is expressed in terms of the system length multiplied by a temperature gradient then , just as in the case of shear , the "entropy production" can be expressed as the square of a current divided by the heat conductivity or the square of a gradient multiplied by the conductivity . The entropy production can be viewed as an artifice designed to preserve the Second Law of Thermodynamics .

In a steady shockwave the influx of cold low-entropy fluid does not match the exiting higher-entropy value . Again there is judged to be entropy produced within the system .

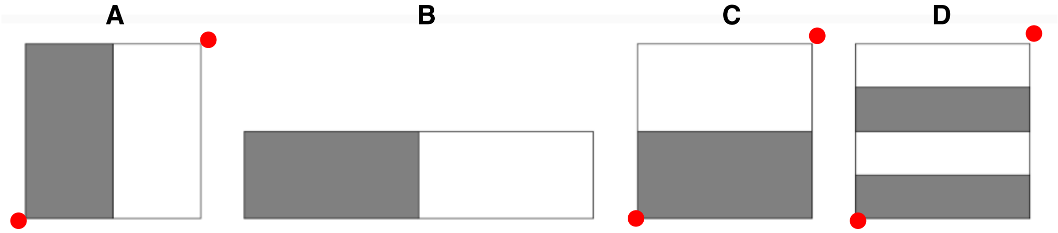
Addendum : Entropy Production

With the advantage of simulation it became possible to study the Gibbs' entropy of simple systems like the Galton Board or the conducting oscillator . What happens is that the distribution function in the phase space becomes fractal , of zero volume , so that the Gibbs' entropy actually does approach (mathematically) minus infinity . Although the formation of the fractal takes a relatively short time to saturate , $20/\lambda$, with single precision ; $40/\lambda$, with double precision ; and $80/\lambda$ with quadruple precision , we see that the limited information provided by our computations does provide steady states with a very small density of states in the phase space .

The overall moral is that extending the concept of entropy to nonequilibrium systems is not a practical activity . On the other hand the fractals produced by nonequilibrium simulations can be viewed and analyzed . Let us look in detail at a simple model for the fractal character of nonequilibrium flows, the Baker Map .

Addendum : Entropy Production via a Modified Baker Map

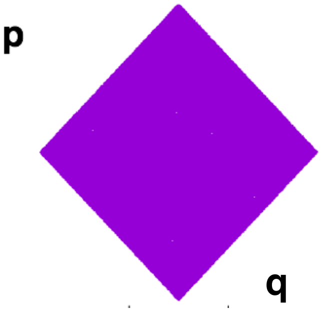
What is the Classic Baker Map ? It maps a square portion of the (x,y) plane onto itself through a shear deformation (A → B) followed by a placement of the right half above the left (B → C) . Locally the horizontal distance between points is doubled : (dx → 2dx) while the vertical distance between points is cut in half : (dy → dy/2) . There are two “fixed points” (•) which are not displaced by the mapping . If one tries to implement the mapping on a digital computer the compression in the y direction loses a “bit” of information each time the map is implemented . [This corresponds to shifting digits to the right .] Expansion In the x direction shifts bits to the left .] D shows the results of two iterations .



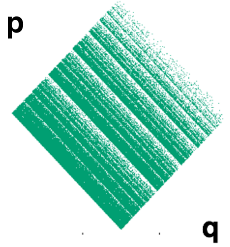
Addendum : Entropy Production via the Baker Map

A time-reversible map which goes everywhere within a two-dimensional phase space but with some regions of the space contracting and some expanding is the Baker Map . The net result is a strange attractor, a fractal object in which the probability density is not smooth and which is more and more concentrated as the resolution of the map is increased. Here is an equilibrium 2 x 2 Baker Map :

```
if(q.lt.p) then
qnew = (5*q – 3*p)/4.0d00 + dsqrt(1.125d00)
pnew = (5*p – 3*q)/4.0d00 – dsqrt(0.125d00)
endif
if(q.gt.p) then
qnew = (5*q – 3*p)/4.0d00 - dsqrt(1.125d00)
pnew = (5*p – 3*q)/4.0d00 + dsqrt(0.125d00)
endif
```



Addendum : Entropy Production *via* the Baker Map



Here is a nonequilibrium 2 x 2 Baker Map in which parts of the square “phase space” expand or shrink by factors of 3 or (3/2) :

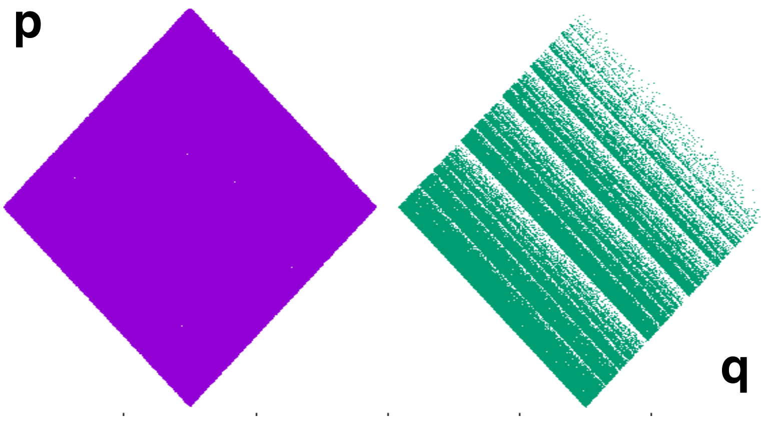
```
if(q.lt.p – dsqrt(2.0d00/9) then
qnew = +(11*q – 7*p)/6.0d00) + dsqrt(49.0d00/18)
pnew = +(11*p – 7*q)/6.0d00) - dsqrt(25.0d00/18)
endif
if(q.gt.p – dsqrt(2.0d00/9) then
qnew = +(11*q – 7*p)/12.0d00) - dsqrt(49.0d00/72)
pnew = +(11*p – 7*q)/12.0d00) - dsqrt( 1.0d00/72)
endif
```

After computing the “new” point (`qnew,pnew`) → (`q,p`) .

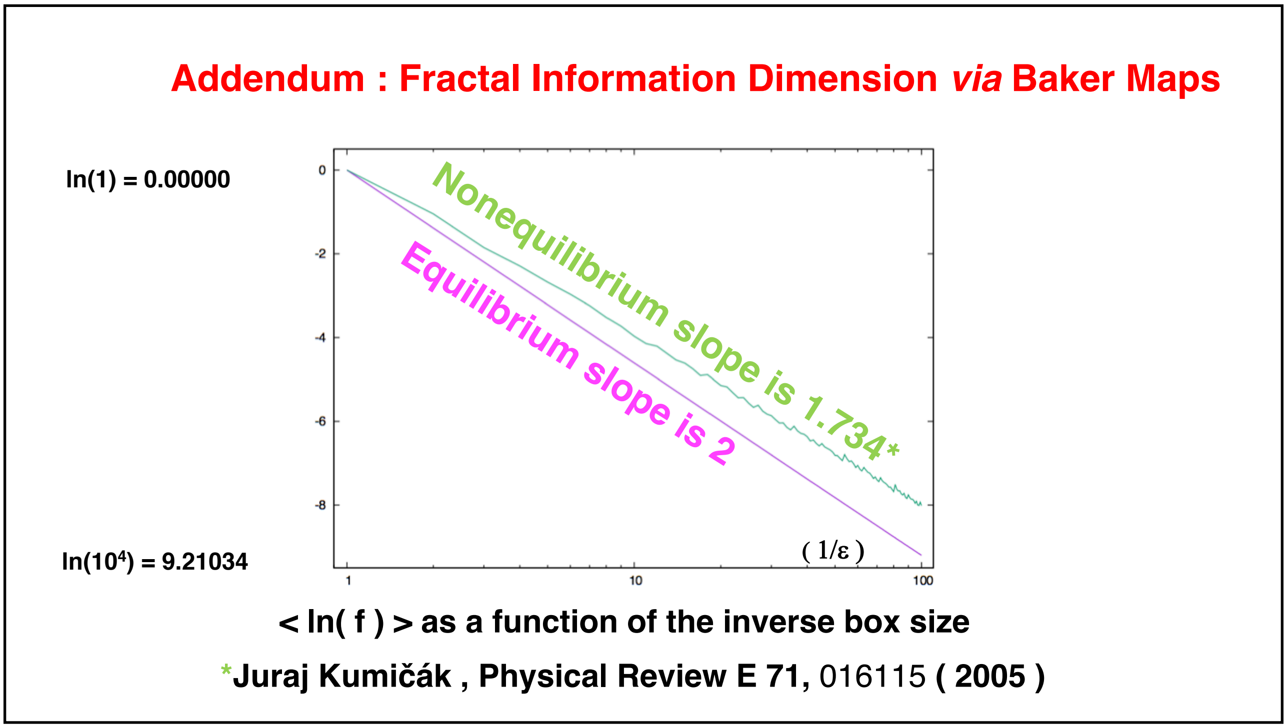
The following graphic shows what happens with half a million Iterations of the equilibrium and nonequilibrium maps .

Addendum : Entropy Production *via* Ergodic Baker Maps

Half a million Iterations of the equilibrium and nonequilibrium maps .



By spanning the space with cells of size ε and measuring the mean value of the logarithm of the probability < ln f > we can determine the dimensionality .



Addendum : Fractal Information Dimension *via* Baker Maps

ln(1) = 0.00000

ln(10^4) = 9.21034

< ln(f) > as a function of the inverse box size

***Juraj Kumičák , Physical Review E 71,** 016115 **(2005)**

Addendum : Entropy Production *via* Ergodic Baker Maps

The "entropy" < ln(f) > has been calculated here using what is called the "Natural Measure", where f is the frequency with which the box is visited . It is perfectly feasible (but not necessarily useful) to define other measures by computing powers of f . The "information dimension" is the one we have calculated . The "correlation dimension" is based on the square of frequency and can alternatively be evaluated by computing the logarithmic dependence of the number of pairs of points in each bin on the bin size ε . This is a little complicated because at small ε the one-dimensional trajectory dimension dominates the statistics . The dimension decreases as the power used in defining it increases . Because information dimension is directly related to Gibbs' entropy it is the one most likely to be useful for statistical mechanics .