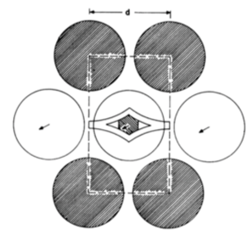
Kharagpur Lecture 7

Statistical Mechanics of Small Systems



Equilibrium Problems :
1. The small-mass cell model for hard particles
2. Einstein model for the harmonic chain and hard rods
3. Hard-disk cell model and correlated cell model
4. Percolation transitions for hard disks and spheres

Nonequilibrium Problems :

5. Galton Board → Multifractal Chaotic Sea , Tori , and Limit Cycles
6. Conducting Oscillator using Ergodic Thermostats / Linear Response Theory
7. 30 Years of Nonequilibrium Fractals
8. Entropy Production and Maximum Entropy

William G. Hoover

Ruby Valley Nevada

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1. Small-Mass Cell Model for Hard Particles

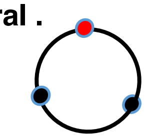
From either of two viewpoints [1] the dynamics of a light particle, or [2] the repeated Monte Carlo moves of an arbitrary particle , there is a well-defined "free volume" . The virial theorem can be applied to relate the free volume to the pressure , $PV/NkT = 1 + (\sigma/4) < s^f/v^f >$, where it is assumed that all configurations of the free volume , bounded by the surface s^f, are of equal probability . This assumption is certainly true for Monte Carlo simulations , and is an accepted result , usually attributed to Sinai , in ergodic theory . My 1978 work for disks , with a single computation for hard spheres led to extensive results (hundreds of data points) for spheres by Sastry *et alii* in 1998 [Molecular Physics 95, 289-297] . The results can be summarized by generalizing the exact one-dimensional result to a two-parameter empirical fit :

$$\int vf(v)dv = \int vdve^{-[v/< v >]}/< v >^2 \rightarrow f(v) = v^a\exp[-v^b] ,$$

Here a and b are close to 1/3 and 1/2 for spheres . For disks a is approximately 0.1 . The application of these ideas to continuous potentials is not so straightforward because the possibility of escape from the cell is always present . On the other hand a model , the "Cell Model" can be implemented numerically as an approximation to the canonical partition function's Nth root . This idea was pursued by Lennard-Jones and Devonshire in 1937-8 (in the Proceedings of the Royal Society of London) and was brought up to date by Magee and Wilding (in Molecular Physics) in 2002 . The Lennard-Jones-Devonshire model is spherically smoothed which adds some arbitrariness to the model . The results they found are interesting . First we will consider simple one- and two-dimensional systems .

Free Volume Calculation for a Periodic One-Dimensional Fluid *

$Q = \int \ldots \int dx_1 dx_2 \ldots dx_N = V^N/(N-1)!$ is the configurational integral .
With periodic boundary conditions it is "obvious" that the
"first" particle can go anywhere along the "volume" V and
that the remaining (N – 1) particles can occupy $V^{N-1}/(N-1)!$



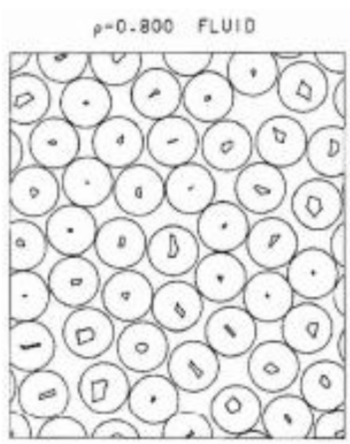
What is the ideal—gas probability of the separation $x_2 - x_1 = v$?
$P(v) = [\, V(V-v)^{N-2}/(N-2)! \,] / [\, VV^{N-1}/(N-1)! \approx Ne^{-Nv/V}/V$,
which is properly normalized : $\int [\, Ne^{-Nv/V} / V \,]\, dv = 1$ and which gives the mean
$\langle v \rangle = \int [\, v\, [\, Ne^{-Nv/V} / V \,]\, dv = (\, V/N \,)$.
If the particles have length σ the calculation is nearly the same and

$\langle v \rangle = (\, V - N\sigma \,) / N$ and $Q^{1/N} = (\, V - N\sigma \,) e / N$
That extra factor of e gives Kirkwood's "Communal Entropy" $S_C = Nk$.

* There is a paper in the 1936 Physical Review by Lewi Tonks on this subject .

1. Small-Mass Dynamics or Gibbs suggest "Cell" Models

The many-body problem can be approximated by a one-body problem . We can select a *typical* many-body configuration and examine its one-body properties . There are special cases in which this idea is exact rather than approximate . This idea can serve as a basis for "cell models" .



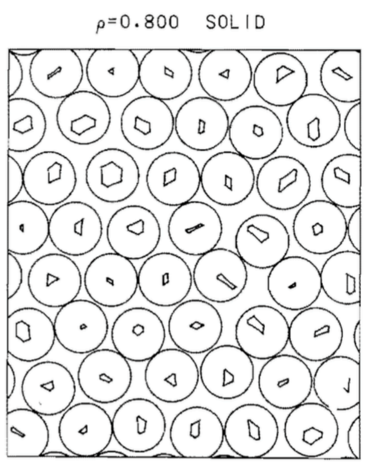
For simplicity we consider hard disks . This simplifies the graphics , the topology , and the dynamics . Disks are a good model system as they exhibit both fluid and solid phases .

To the left is an equilibrated fluid configuration of 48 hard disks . The boundary conditions are periodic so that any disk leaving the box is simultaneously introduced on the opposite side . At this density , 4/5 that of the "triangular" close-packed lattice , the solid phase is more stable than the fluid .

Such an equilibrium configuration can be obtained from molecular dynamics or Monte Carlo simulations . The two approaches produce identical results with microcanonical and canonical configurations identical .

1. Small-Mass Cell Model for Hard Particles

Here the 48 disks have a solid configuration . The free volume is $0.0261\sigma^2$ for the solid while the fluid free volume is considerably smaller , $0.0218\sigma^2$. These free volumes have a direct connection to equilibrium properties, including the pressure and the chemical potential . Disk diameter = σ .



Here is a solid configuration of 48 hard disks . The boundary conditions are periodic so that any disk leaving the box is introduced on the opposite side . At this density , 4/5 of the close-packed , the solid phase is more stable than the fluid . The particle speeds are of order $\sqrt{(kT/m)}$ and have the same distribution in either of the phases .

At each particle's location the "free volume" v_f it can access is drawn in . If one of the particles were "light", much less massive than the others , this is the area which it would sweep out over a long time . In classical mechanics the phase integral $\iint dqdp$ is a product $\int dq \times \int dp$ whether or not the phase volume is weighted with the Boltzmann factor . Microcanonical and canonical configurations are exactly the same . Looking at a configuration doesn't reveal any differences between the two ensembles . This is also true of the Maxwell-Boltzmann velocity distributions .

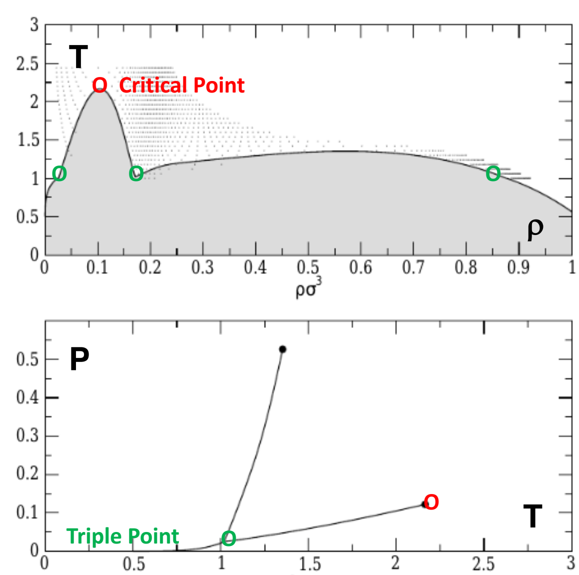
1. Magee-Wilding Cell Model for Lennard-Jones ϕ

Magee and Wilding (2002) explored the spherically smoothed LJD cell model using the 12-6 potential :

$$\phi (r) = 4 \varepsilon [(\sigma /r)^{12} - (\sigma /r)^6] .$$

Here ε is the well depth and σ is the collision diameter . They found the relatively bizarre phase diagram shown here with two coexistence regions (only one of these had been found by LJD) , along with two critical points . Gholamreza Vakili-Nezhaad extended this work by varying the coordination number, adding more complexity to a model nearly 80 years old !

In the plots the units of T are (ε / k) , of P are (ε/σ^3) , while those of ρ are (m/σ^3) . Evidently there is food for thought in the model . We next pursue simpler applications, hard rods , disks , and spheres , as well as crystal lattices held together with Hooke's-Law spring interactions , with $\phi (r) = \kappa(r - d)^2/2$, where d is the restlength of the springs .



2. Einstein Model for the Harmonic Chain and Hard Rods

Starting at one end of the harmonic chain and integrating $\exp[-\kappa\delta x^2/2kT]d\delta x$ gives the exact limiting result for the configurational Integral : $Z_q = (2\pi kT/\kappa)^{(N/2)}$.

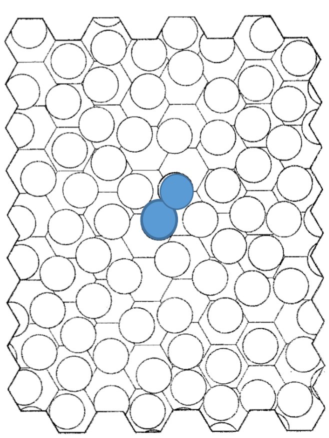
Einstein's approximation , picking one oscillator in the middle , gives a smaller result : $\exp[-2\kappa\delta x^2/2kT]d\delta x \rightarrow (\pi kT/\kappa)^{(N/2)}$, so that the oscillator integral is too small by $\sqrt{2}$. The exact entropy exceeds the Einstein model by 0.3466 Nk .

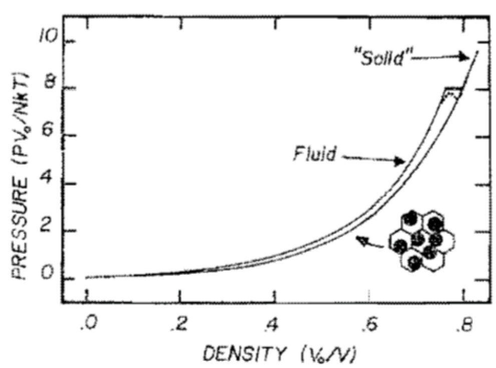
The hard-rod configurational integral gives a similar result . In the exact case there is an iterated integral over a space $(V-N)^N$. If the particles remain ordered then the result is $Z_q = (V-N)^N/N!$ The result is exactly the same if the particles are allowed *any* ordering and then the integral is corrected for indistinguishability . The exact (Stirling limit) result $Z_q = [(V/N)-1]^N e^N$, is bigger than the cell model estimate $[(V/N)-1]^N 2^N$ by a factor of 1.3591 , similar to 1.4142 . The entropy exceeds the Einstein value by 0.30685 Nk . Stirling's approximation : $N! \approx \sqrt{(2\pi N)}(N/e)^N + O(1/N)$.

The one-dimensional models can be worked out easily . In two dimensions the harmonic crystal entropy (using the triangular lattice , where each particle has six nearest neighbors) exceeds that of the Einstein model by 0.27326 Nk .

3. Hard-Disk Cell Model and the Correlated Cell Model

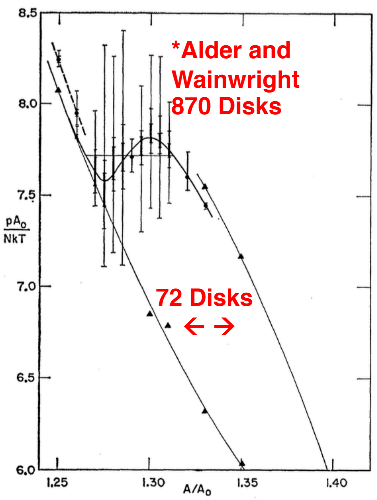
The two-dimensional hard-disk model is complicated , even for the triangular (solid) lattice . The entropy of the solid is most easily computed by integrating The isothermal equation of state from the low-density limit to high density using single-occupancy boundary conditions (a trick !) * . $TdS = dE + PdV = PdV$.

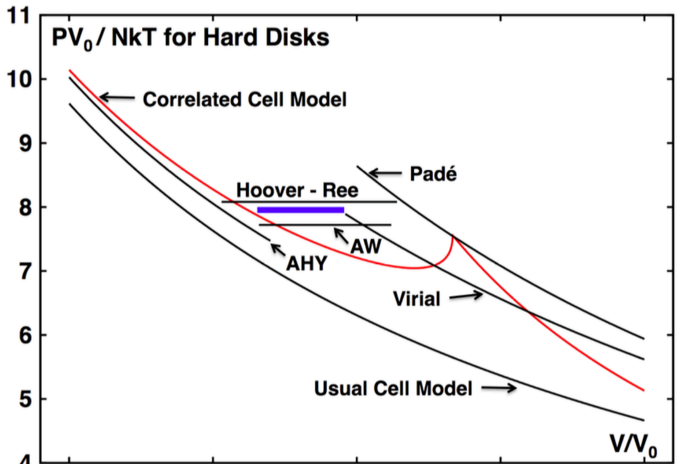




*** Journal of Chemical Physics 49,** 3609-3617 **(1968) .**
[The Communal Entropy comes in very gradually .]

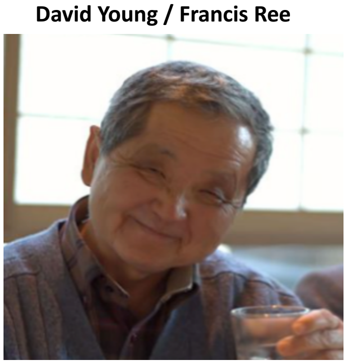
3. Hard-Disk Cell Model and Correlated Cell Model





* Alder and Wainwright, Physical Review 127 , 359-361 (1962) .
* M. Engel , J. A. Anderson , S. C. Glotzer , M. Isobe , E. P. Bernard , and W. Krauth , arXiv 1211.1645 .

David Young / Francis Ree



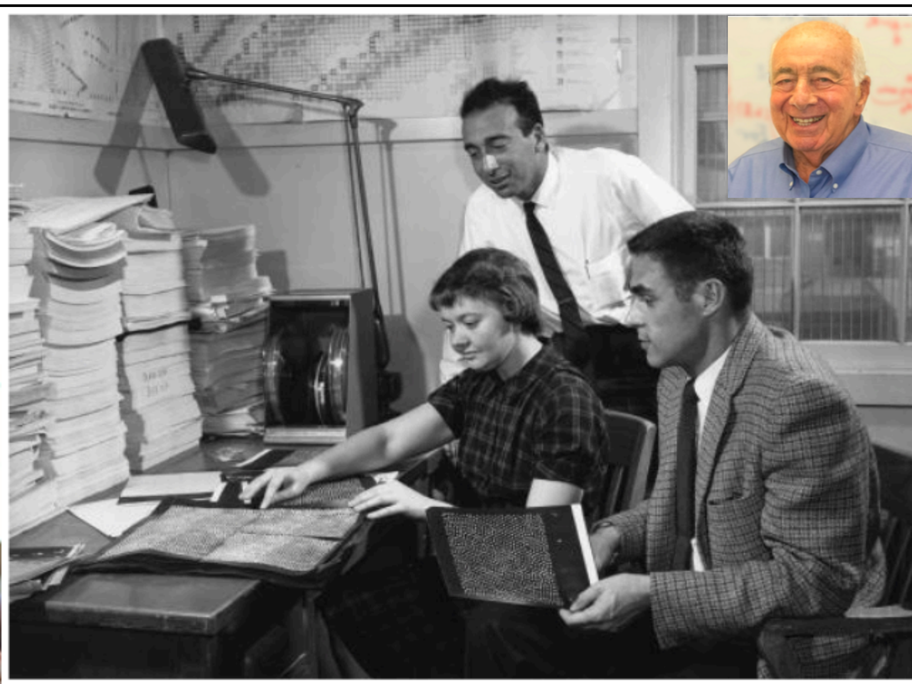
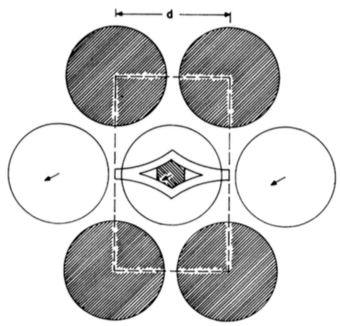
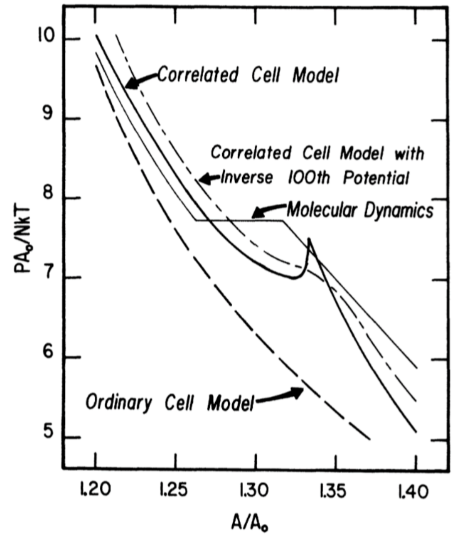


Photo 1 Mary Ann Mansigh, Berni Alder, and Tom Wainwright

3. Hard-Disk Cell Model and the Correlated Cell Model





* **Alder , Hoover , and Wainwright , Physical Review Letters 11 ,** 241-243 **(1963) .**

3. Hard-Disk Cell Model → Correlated Cell Model

$$pA/NkT = \partial(\ln a_f)/\partial(\ln A) = \partial(\ln a_f)/\partial(\ln d^2)$$

$$\boxed{a_f = (3d^4)^{1/2} - \tfrac{1}{2}(4d^2 - d^4)^{1/2} - 2\sin^{-1}(\tfrac{1}{4}d^2)^{1/2}}$$

$$- \tfrac{1}{2}(12d^2 - 9d^4)^{1/2} + 2\cos^{-1}(3d^2/4)^{1/2}$$

$$\text{for } 1 < d^2 < \tfrac{4}{3},$$

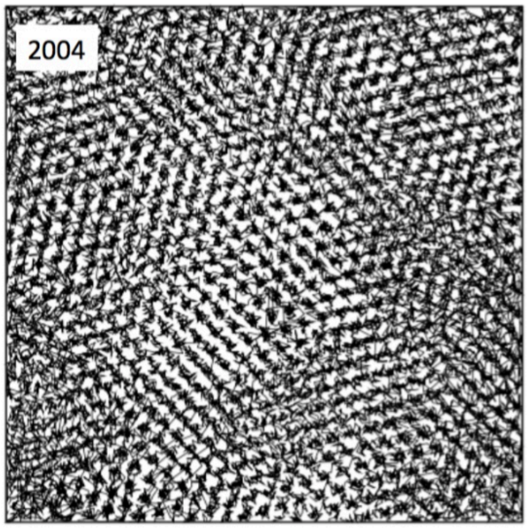
Low Density :
← $d^2 > (4/3)$

Correlated Cell Model Free Volumes generate a van der Waals'-like pressure-volume loop .

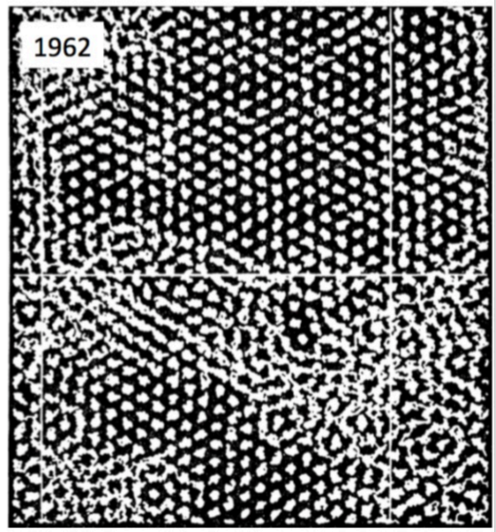
* **Alder , Hoover , and Wainwright , Physical Review Letters 11 ,** 241-243 **(1963) .**

3. Evidently the Correlations seen in Movies Characterize "Hexatic" Phases .

Ronen Zangi + Stuart Rice



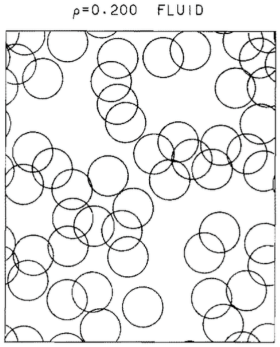
Alder + Wainwright



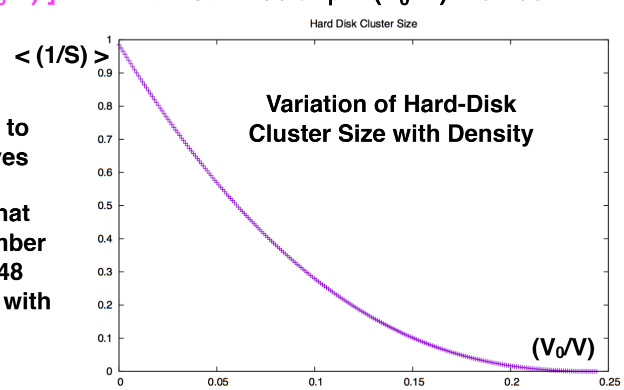
4. The Percolation Transition for Hard Disks

It is evident that the free volume is extensive at low density, $v_f \rightarrow V - (N-1)(\pi\sigma^2)$. Likewise at the high density of 0.8 relative to close packing the free volume is intensive , $v_f \propto (V/N)[\,1 - \sqrt{(V_0/V)}\,]^2$. This observation suggests a transition, called the "percolation transition". The transition can be quantified by measuring the cluster size S : $\langle 1/S \rangle = 28.8\,[\,0.245 - (V_0/V)\,]^{2.4} \rightarrow 1/\langle 1/S \rangle = 56$ at $\rho = (V_0/V) = 0.200$.

ρ=0.200 FLUID



← To the left the fit to simulation data gives an average cluster size of 56 , somewhat larger than the number of particles in this 48 particle simulation with seven clusters .



4. Exact Cell Models and Percolation for Hard Particles

We have seen that both the "light-particle" dynamical approach [1] and the Monte Carlo statistical approach [2] lead to the conclusion that the pressure (or momentum flux) can be expressed in terms of the free volume v_f and its surface area s_f (a length for disks) :

$$(PV/NkT) = 1 + (1/4) < s_f / v_f > = 1 + (1/4) < s_f > / < v_f > .$$

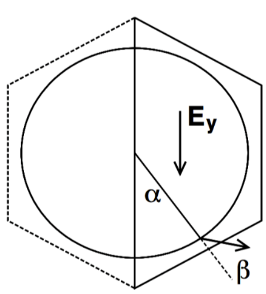
There is a comprehensive table in "Exact Hard-Disk Free Volumes", Journal of Chemical Physics 70, 1837-1844 **(1969) showing the quantitative agreement of these equations of state with the many-body simulations . A generation later Srikanth Sastry *et alii* * carried out a comprehensive study of the hard-sphere analog using a division of the many-body configuration into Voronoi cells to partition the free volumes into manageable pieces .**

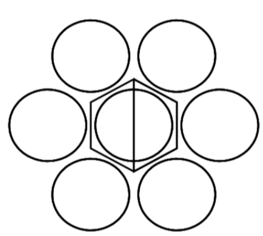
Les Woodcock , in the 2012 Journal of the American Institute of Chemical Engineers , points out that hard spheres have *two* very different "percolation transistions" . The lower-density excluded-volume percolation occurs when a single cluster of spheres excludes a volume extending all the way across the system . The higher-density percolation occurs when the volumes available for another sphere become a disjoint set of isolated holes .

*** = Truskett , Debenedetti , Torquato , and Stillinger , Molecular Physics 95 ,** 289-297 **(1998) .**

5. Galton Board → Multifractal Chaotic Sea , Tori , and Limit Cycles

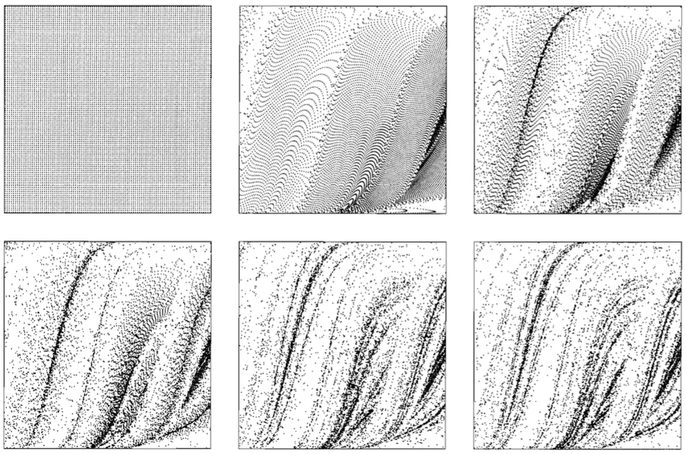
$$dx/dt = u \; ; \; du/dt = -\zeta u \; ;$$
$$dy/dt = v \; ; \; dv/dt = -E - \zeta v$$



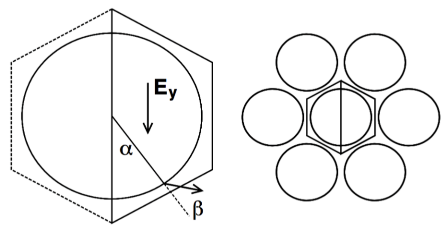


Clint Sprott (2015)

5. Phase-space cross sections develop in time*



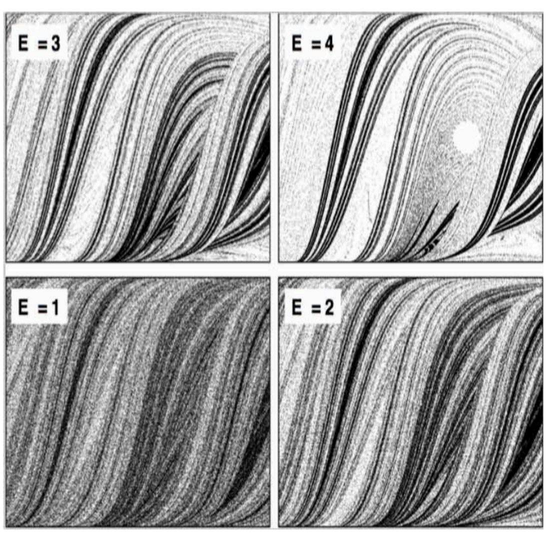
$$dx/dt = u \; ; \; du/dt = -\zeta u \; ;$$
$$dy/dt = v \; ; \; dv/dt = -E - \zeta v$$



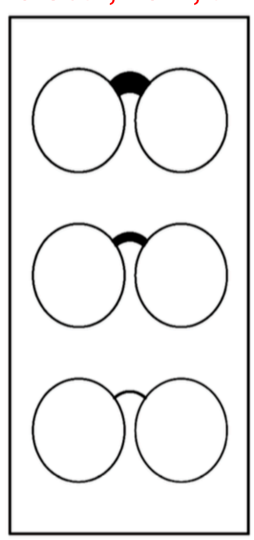
* sin(β) versus α for 0 , 1 , 2 , 3 , 5 , and 10 collisions of 10 000 initial conditions

5. Galton Board → Multifractal Chaotic Sea , Tori , and Limit Cycles

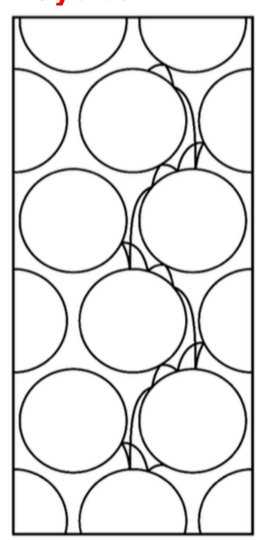
-1 < sin(β) < +1



0 < α < π



Torus



Limit Cycle

5. Fractal Analysis of the Galton Board Sections

The fractals can be analyzed in terms of "measures" based on $\#^a$ where there are # points in the bins and the exponent a varies (here) from 0 to 10 . The most useful measure is the "natural measure" # with a = 1 .

Fractals have *fractional* dimensionality in the sense that the number of points # in the vicinity r of an arbitrarily chosen phase-space point varies as a *fractional* power of r . The power is 1.832 in the Galton Board problem where the field strength is 3 .

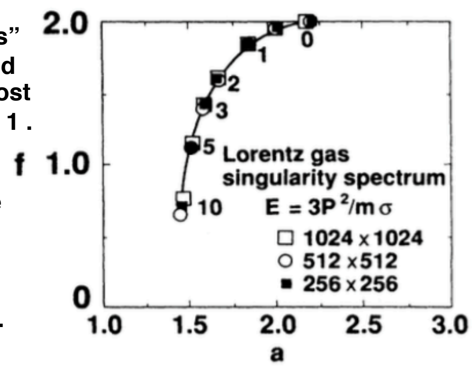


FIG. 6. Spectrum of fractal dimension $f(a)$ found here for the nonequilibrium system of Figs. 4 and 5 using a field strength of $3P^2/m\sigma$ and 100 000 000 collisions. Points shown are labeled according to the number of bins spanning $(\alpha, \sin\beta)$ space, 256^2, 512^2, and 1024^2. The q values, in the range from 0 to 10 are indicated, except for $q=\frac{1}{2}$.

The numerical data show that the apparent dimension varies only a little with the size of the mesh .

5. The Deviations from Equilibrium are Quadratic *

Were it the case that the deviations from equilibrium were smooth and described by a Taylor's series we would expect to find a quadratic dependence of dimensionality on on the field strength E . This idea is not too far from true .

Keep in mind that conductivity varies in a complicated way on field strength . Fractals have structure on all scales , which makes analytic dependences unlikely .

$D_1 = \Sigma \mu_1 \ln(\mu_1) / \ln\delta$

$D_2 = \Sigma \mu_2 \ln(\mu_2) / \ln\delta$

$\alpha_2 = \Sigma \mu_2 \ln(\mu_1) / \ln\delta$

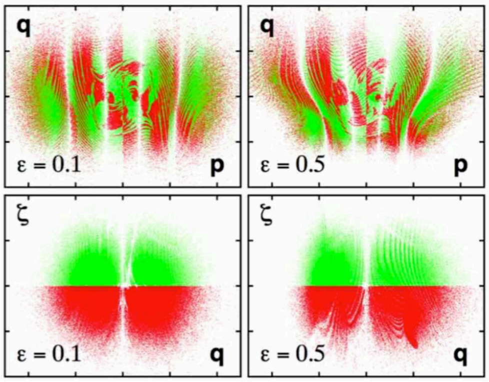
Here the measures are based on [1] *points* or on [2] *pairs* .

TABLE I. Information and correlation dimensions D_1 and D_2 for 100 000 000 hard-disk collisions using 512×512 bins. The a value corresponding to the correlation dimension $a_2(q=2)$ is shown also. The "fit" results for these dimensions all give the result of a quadratic dependence between zero field and $E=P^2/m\sigma$. For comparison, the results for $E=3P^2/m\sigma$ are also shown, though these exhibit significant deviation from the small-field quadratic behavior.

	Dimensionless field strength: $Em\sigma/P^2$					
	0.000	0.250	0.500	0.750	1.000	3.000
D_1	2.000	1.998	1.995	1.988	1.979	1.832
Fit	2.000	1.999	1.995	1.988	1.979	1.81[a]
D_2	1.999	1.994	1.980	1.955	1.920	1.583
Fit	2.000	1.995	1.980	1.955	1.920	1.28
a_2	2.000	1.995	1.985	1.966	1.940	1.656
Fit	2.000	1.996	1.985	1.966	1.940	1.46

* Hoover and Moran, Physical Review A **40**, 5319-5326 (**1989**) .

6. Conducting Oscillator Using Ergodic Thermostats *



10 x 8 Nonequilibrium Cross Sections

$T(q) = 1 + \epsilon \tanh(q) \; ; \; 0 < \epsilon < 1 \longleftrightarrow 0 < T(q) < 2$

$$\dot{q} = p \; ; \; \dot{p} = -q - \zeta[\, 1.5p - 0.5(p^5/T^2) \,] \; ;$$

$$\dot{\zeta} = 1.5[\, (p^2/T) - 1 \,] - 0.5[\, (p^6/T^3) - 5(p^4/T^2) \,]$$

In the equilibrium case, ε = 0 , the cross section of the distribution is a Gaussian . The white spaces indicate portions of the section where the trajectory is parallel to the plane . For example (dp/dt) vanishes when q and p are both zero . The white spaces are called "nullclines" .

The colors show λ > 0 and λ < 0 .

* **arXiv 1507.08302 (2015)**

6. Conducting Oscillator Using Ergodic Thermostats *

As a bit of review let's show that these three equations are consistent with an extended Gibbs' canonical distribution with T = 1 .

$$\dot{q} = p \; ; \; \dot{p} = -q - \zeta[\, 1.5p - 0.5(p^5/T^2) \,] \; ;$$

$$\dot{\zeta} = 1.5[\, (p^2/T) - 1 \,] - 0.5[\, (p^6/T^3) - 5(p^4/T^2) \,]$$

Suppose that $f(q, p, \zeta) = e^{-q^2/2} e^{-p^2/2} e^{-\zeta^2/2}$ and apply Liouville's Theorem .
The three-dimensional Gaussian will be a stationary solution provided that

$$-(\partial \dot{p}/\partial p) + q\dot{q} + p\dot{p} + \zeta\dot{\zeta} = 0 \; .$$

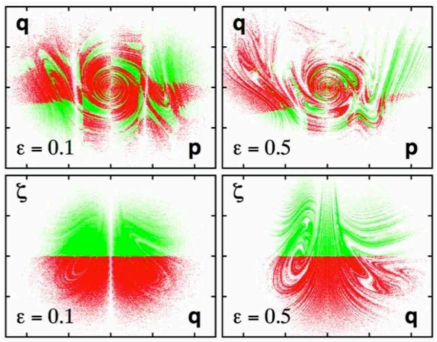
Writing out these four terms in full gives :

$$\overset{A}{1.5\zeta} - \overset{B}{2.5\zeta p^4} + \overset{C}{qp} + p(\overset{C}{-q} - \overset{D}{1.5\zeta p} + \overset{E}{0.5\zeta p^5}) + \zeta[\, \overset{A}{-1.5} + \overset{D}{1.5p^2} + \overset{B}{2.5p^4} - \overset{E}{0.5p^6} \,] \; .$$

This sum is precisely zero and numerical work indicates that the equations are ergodic .

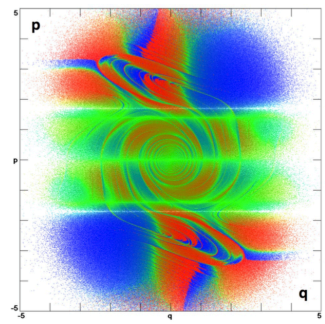
* **arXiv 1507.08302 (2015) has all the details .**

6. Conducting Oscillator Using Ergodic Thermostats*



$$\dot{q} = p \; ; \; \dot{p} = -q - \zeta[\, 0.05p + 0.32(p^3/T)\,]$$

$$\dot{\zeta} = +0.05[\, (p^2/T) - 1\,] + 0.32[\, (p^4/T^2) - 3(p^2/T)\,]$$



10 x 8 Nonequilibrium Cross Sections

$T(q) = 1 + \epsilon \tanh(q) \; ; \; 0 < \epsilon < 1 \longleftrightarrow 0 < T(q) < 2$

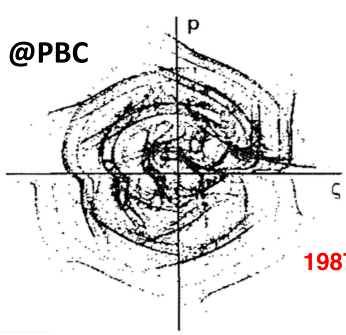
10 x 10 Equilibrium Cross Section, T = 1

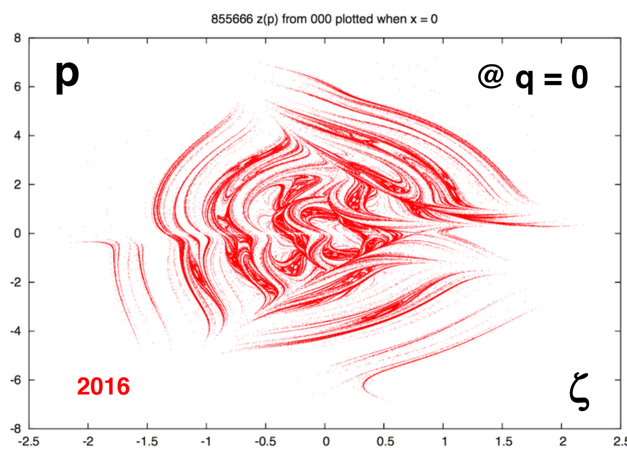
* arXiv 1507.08302 (2015) . This oscillator model , the 0532 Model , is likewise ergodic .

7. Nonequilibrium Fractals : Galton Staircase*

$(dq/dt) = p$
$(dp/dt) = 1 - 0.3 \sin(q) - \zeta p$
$(d\zeta/dt) = 0.1\, (p^2 - 1)$

@PBC



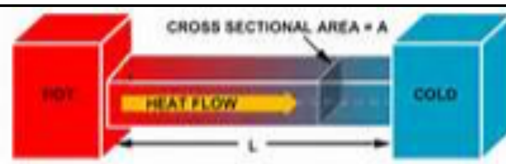


* Hoover , Posch , Holian , Gillan , Mareschal , Massobrio, 1987 Molecular Simulation

8. 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 $\{ -\zeta p^2 \}$ 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, $dS/dt = -(V/T)dQ/dt - P_{xy}V(du_x/dy)/T$. 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 .

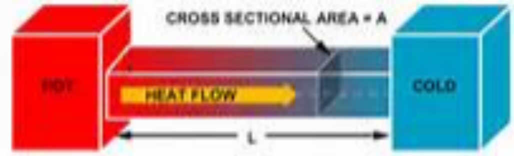
8. Addendum : Entropy Production



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 $\langle Q \rangle [1/T_H - 1/T_c] < 0$. 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 , or said to be , entropy produced within the system . It is useful to remember that entropy is a property of *distributions* of systems .

8. Addendum : Entropy Production



There is a "fly in the ointment" associated with Entropy Production .

If it really were true that entropy is generated inside a fluid whenever there is a shear stress or a heat flux we would expect to see entropy increase even in an equilibrium fluid . The lack of any entropy change at equilibrium guarantees the artificiality of the "production" concept .

The different points of view (microscopic , a particle picture with reversible equations of motion and continual fluctuations) and (MACROscopic , with fields instead of point particles and with at least partially irreversible motion and energy equations) are only approximately consistent with each other . Any consistency requires some averaging , in time , space , or both , and will never lead to perfect agreement .

8. 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 , perhaps $20/\lambda$ with single precision , $40/\lambda$ with double , and $80/\lambda$ with quadruple , we see that the limited information provided by computation *does* provide a steady state with a very small density of states in the phase space .

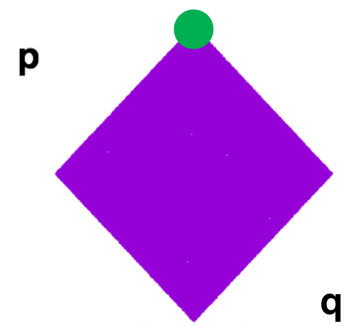
The overall moral is that extending the concept of entropy to nonequilibrium systems is not a practical activity* . On the other hand the fractals produced by nonequilibrium simulations can be viewed and analyzed . Let us look in detail at a simple model for the fractal character of nonequilibrium flows,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

* There is a nice article in the 2011 volume of Entropy by R M Velasco, Leo G-C Scherer and F J Uribe .

8. 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 the equilibrium Baker Map :

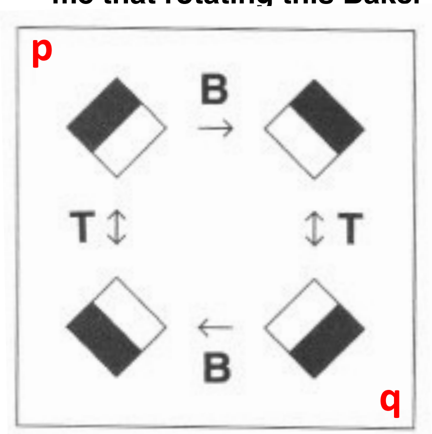
```
if(q.lt.p) then
qnew = +1.25*q - 0.75*p + dsqrt(1.125d00)
pnew = -0.75*q + 1.25*p – dsqrt(0.125d00)
endif
if(q.gt.p) then
qnew = +1.25*q - 0.75*p - dsqrt(1.125d00)
pnew = -0.75*q + 1.25*p + dsqrt(0.125d00)
endif
```



There is a "fixed point" where $(q,p) = (0,\sqrt{2})$. Can you find another ?

8. Addendum : Entropy Production *via* the Baker Map *

Here again if the Baker Map B which preserves area . Bill Vance pointed out to me that rotating this Baker Map 90° makes it time-reversible T , as shown here :

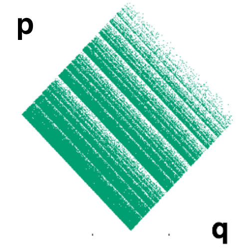



```
if(q.lt.p) then The Black region of the top B map
qnew = +1.25*q - 0.75*p + dsqrt(1.125d00)
pnew = -0.75*q + 1.25*p – dsqrt(0.125d00)
endif
if(q.gt.p) then The White region of the top B map
qnew = +1.25*q - 0.75*p - dsqrt(1.125d00)
pnew = -0.75*q + 1.25*p + dsqrt(0.125d00)
endif
```

The combination of four mappings BTBT is the "Identity Map". If the area is not preserved by such a mapping the resulting "Dissipative Baker Map" generates a multifractal (q,p) object .

Here is an interesting reference → *Juraj Kumičák , Physical Review E 71, 016115 (2005)

8. Addendum : Entropy Production *via* the Baker Map



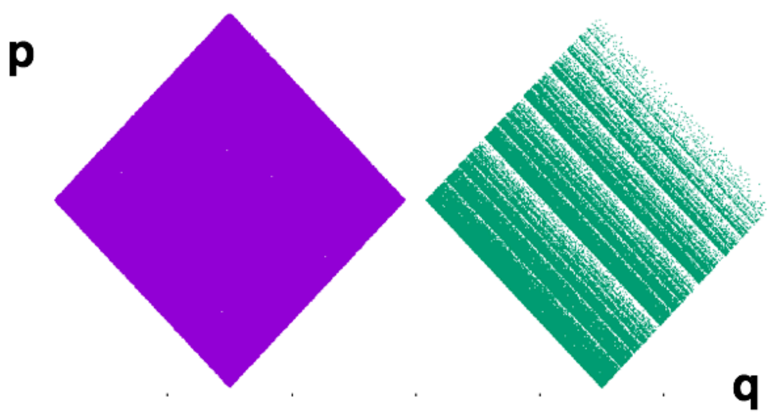
Here is a nonequilibrium 2 x 2 Baker Map in which parts of the square "phase space" expand or shrink by factors of 3 and 3/2 :

```
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
```

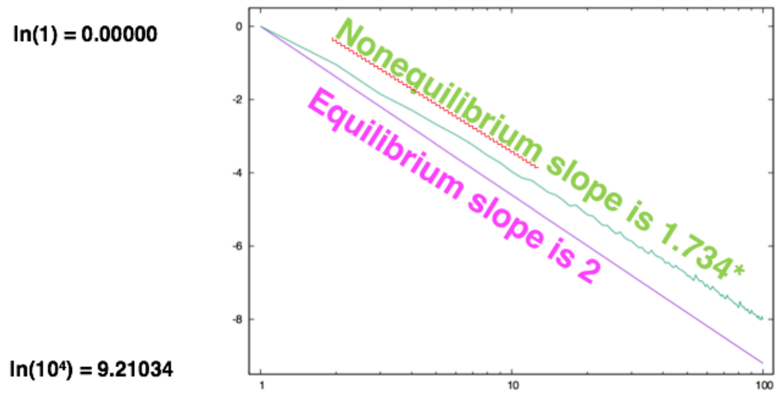
After computing the "new" point (`qnew,pnew`) → (`q,p`) .
The following graphic shows what happens with half a million iterations of the equilibrium and nonequilibrium maps .

Addendum : Entropy Production *via* Ergodic Baker Maps

Half a million Iterations of the equilibrium and nonequilibrium maps .



Addendum : Fractal Information Dimension *via* Baker Maps



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

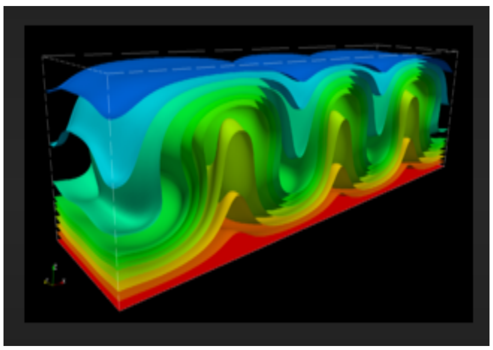
*Juraj Kumičák , Physical Review E 71, 016115 (2005)

8. 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 . 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 .

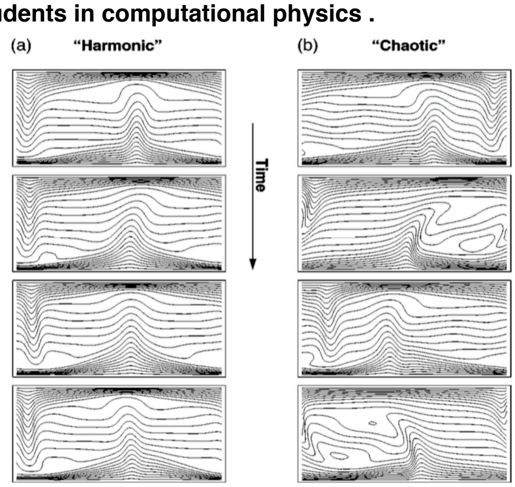
Addendum : Maximum Entropy as a Predictor

Edwin Jaynes (1922-1998) believed that "entropy" – k < ln(f) > could be used to predict *nonequilibrium* probabilities, not just equilibrium ones . His maximum-entropy principle suggests to me that he would expect larger-entropy situations more likely to be observed than their smaller-entropy relatives. A good test of this idea is the degenerate Rayleigh-Bénard problem .



Addendum : Maximum Entropy as a Predictor

Vic Castillo (at the Lawrence Livermore National Laboratory) did his 1999 PhD work with Bill in the University of California's Department of Applied Science at Livermore . He studied the Rayleigh Bénard problem with an emphasis on entropy and chaos . Many of his interesting publications can be found on Research Gate . Here Vic is mentoring new students in computational physics .



8. Maximum Entropy as a Structural Predictor ?

We know that gravity and temperature can interact to cause Rayleigh-Bénard instability . An enclosed fluid , heated from below with vertical gravity , can generate convection currents . We can imagine a competition between Fourier's Law , where the entropy production depends on the temperature gradient , and convection currents , which add dissipation from velocity gradients . Because we expect a stationary state when the boundary temperatures are fixed we can measure the entropy production in two ways :

[1] Q [($1/T_{COLD}$) – ($1/T_{HOT}$)] , from heat transfer at the top and bottom boundaries .
[2] Integrate the local production over the entire volume V : $\int dV\,(\sigma : \nabla u - q\cdot\nabla \ln T) / T$.

These two methods agree precisely for the following model :

Solve the Eulerian Fluid Equations :

$$(\partial\rho/\partial t) = -\nabla\cdot(\rho v),$$

$$(\partial v/\partial t) = -v\cdot\nabla v + (1/\rho)\nabla\cdot\sigma + g,$$

$$(\partial e/\partial t) = -v\cdot\nabla e + (1/\rho)[\nabla v:\sigma - \nabla\cdot Q].$$

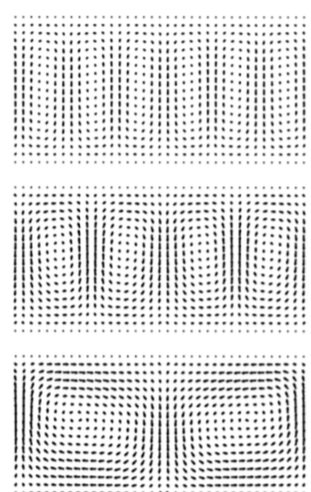
Simple Constitutive Fluid Model :

PV = NkT with constant $\nu = (\eta/\rho)$ and κ . Centered differences in space with v and e at nodes and ρ in cell centers ; g = $\Delta T/H \rightarrow$ constant density with a constant temperature gradient .

8. Maximum Entropy Production as a Structural Predictor

TABLE I. The horizontal and vertical contributions to the kinetic energy per unit mass, the internal energy per unit mass, the boundary heat flux, and the small-amplitude growth rate of the kinetic energy, multiplied by the system width W, are given for a series of fully converged solutions at a Rayleigh number of 40 000. Two-roll, four-roll, and six-roll solutions are compared. $W=2H$. $N=2H^2$. In the continuum limit energies vary as N, traversal times, diffusion times, and dissipation rates as $N^{1/2}\propto H$.

Rolls	K_x/Nm	K_y/Nm	E/Nm	$Q_{boundary}$	W/τ
2	0.003730	0.00357	1.014	0.0120	1.42
4	0.001139	0.00410	1.018	0.0118	1.70
6	0.000274	0.00226	1.012	0.0106	1.25

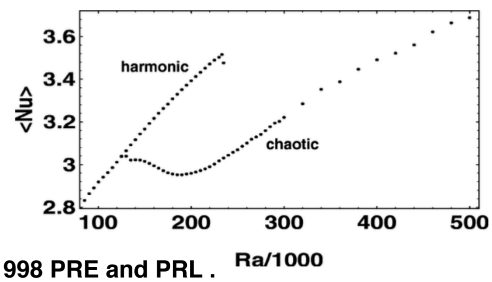


[There are several papers by Vic Castillo, Oyeon Kum, Harald Posch, and the Hoovers in the late 1990s]

8. Maximum Entropy as a Structural Predictor *

In two dimensions the two-roll and four-roll patterns were stable to machine acccuracy while the six-roll solution is unstable at a time of 470 sound-traversal times , after which it changes to either the two-roll or the four-roll structure . In three dimensions an intermediate pattern forms in which the orientation of the rolls is rotated 45 degrees .

Based on energy , heat flux , and Lyapunov growth rate the Table suggests that the six-roll structure is most stable . Evidently what happens depends upon the initial conditions . For our constitutive model Ra = $(H/\nu)^2$ with 2300 the threshold for convection . For Rayleigh numbers above 140 000 oscillating and chaotic solutions coexist , with the oscillating rolls providing 20% more heat transfer with the result about three times greater than the heat transfer due to Fourier conduction :

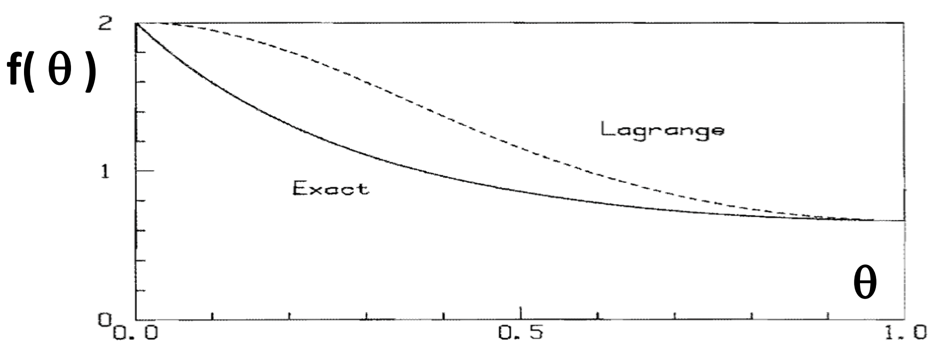


Because the continuum solutions are no doubt correct for “large systems” they strongly suggest that molecular dynamics loses ergodicity for large systems .

* Castillo-Hoover references are in the December 1998 PRE and PRL .

8. Maximum Entropy as a Structural Predictor

In **Nonlinear Conductivity and Entropy in the Two-Body Boltzmann Gas in the Journal of Statistcal Physics 42,** 587-600 **(1986) I compared the solution of the Boltzmann equation for two hard disks, driven in opposite directions by a field, to the “Information Theory” distribution corresponding to the same current . The two solutions are quite different, indicating that Information Theory is unreliable . θ is the direction of the velocity relative to the field .**



Statistical Mechanics of Small Systems

EQUILIBRIUM IDEAS :

1. The small-mass limit → cell model , the Einstein model for a chain of oscillators .
2. Tonks' hard-rod model validates Mayers' theory
3. Hard disks validate cell-model ideas .
4. Percolation transition → interesting topology .

NONEQUILIBRIUM IDEAS :

5. Galton Board → Fractal Sea , Tori , and Limit Cycles .
6. Conducting oscillator → 7. Fractals , Linear response .
8. Maximum Entropy seems to be a Failure .