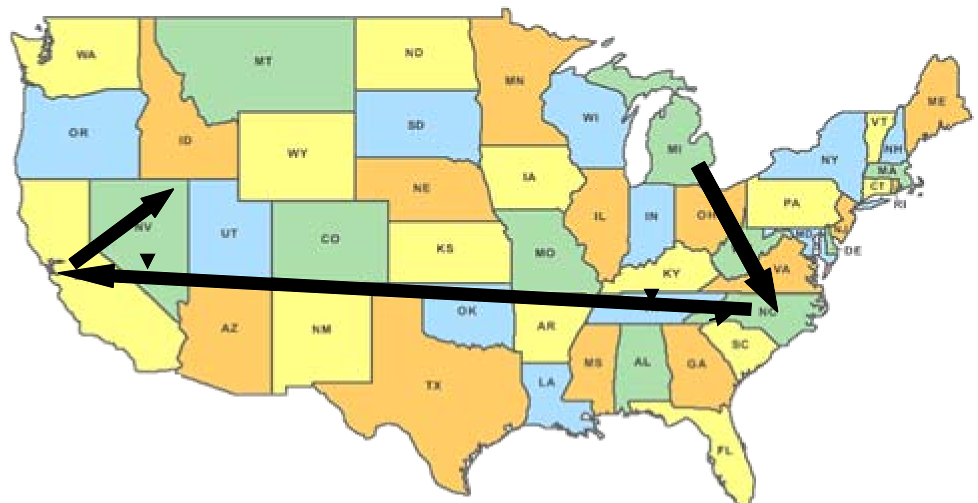
Squares, Cubes, Disks, Spheres

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



Ruby Valley Research Institute
Highway Contract 60, Box 601
Ruby Valley 89833 Nevada USA

Ruby Valley Neighbors

Local Ruby Valley Industry

MICRO-BREWED IN NEVADA'S HIGH COUNTRY

RUBY MOUNTAIN

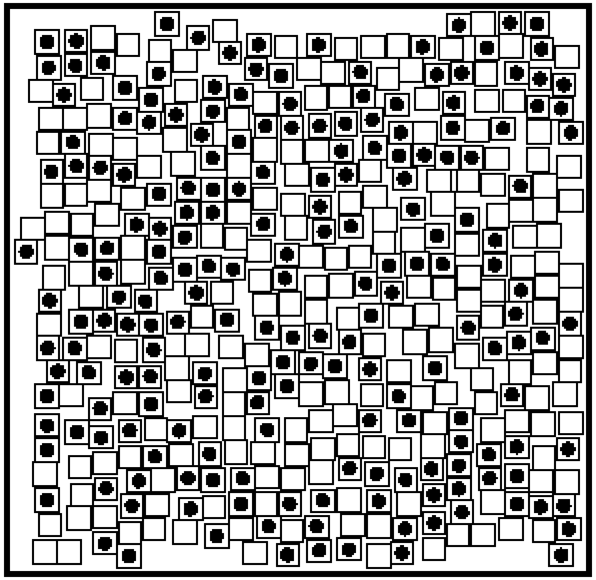
BREWING COMPANY

VIENNA STYLE

LAGER

Hard Parallel Squares

N = 400; V = 600



$$\phi(x,y) = \phi(x)\,\phi(y)$$

so that

$$F(x,y) = F(x) \text{ or } F(y)$$

Squares, Cubes, Disks, and Spheres (1950s-2009)

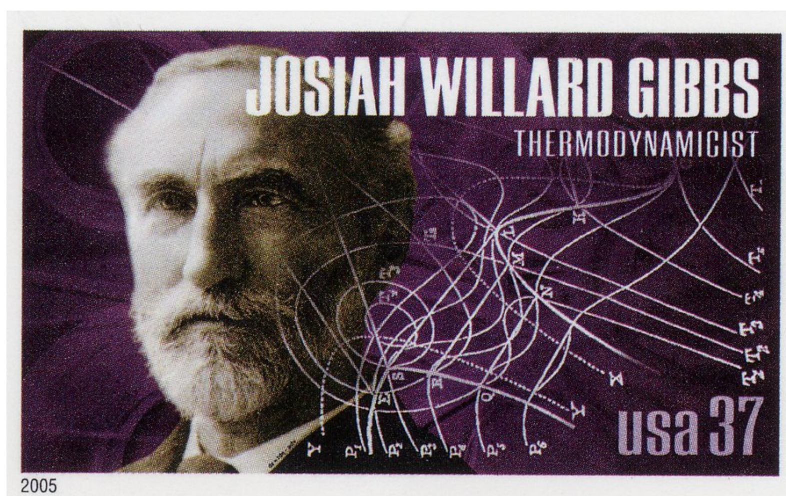
William G. Hoover and Carol G. Hoover
Ruby Valley, Nevada, USA

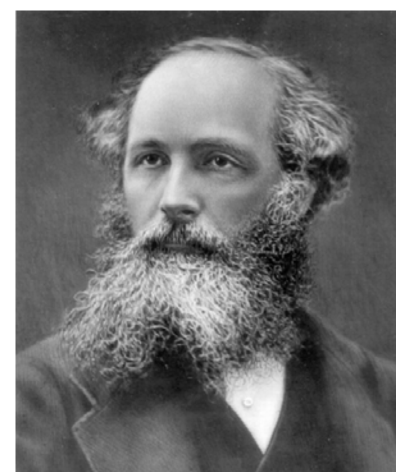
1. Statistical Mechanics for Hard Squares/Cubes
2. Low-Density Virial Equation of State
3. High-Density Free Volumes and Cell Models
4. Single-Speed Molecular Dynamics
5. Results versus Virial Series and Cell Models
6. Melting and the “Region of Confusion”
7. Entropy from Single-Occupancy Dynamics
8. Conclusions and Future Work

Statistical Mechanics Pioneers

Maxwell+Boltzmann → Kinetic Theory, Temperature, and the Virial Theorem

Gibbs → Statistical Mechanics, Partition Functions, and Distribution Functions

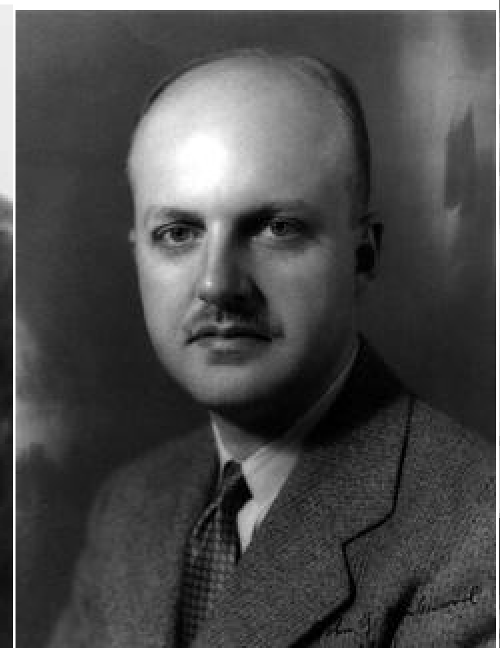




Virial Series and Cell Theories

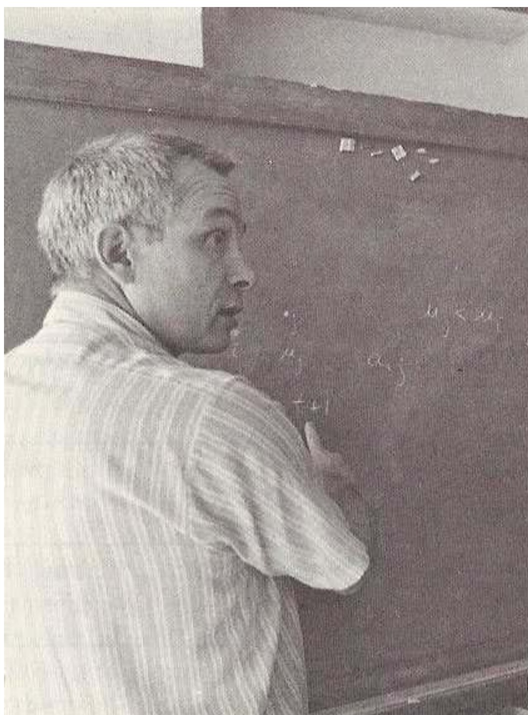
- Mayers → Virial Series from Gibbs' Q_N
- Eyring+Hirschfelder → Cell Models
- Kirkwood → Single-Occupancy Q_N

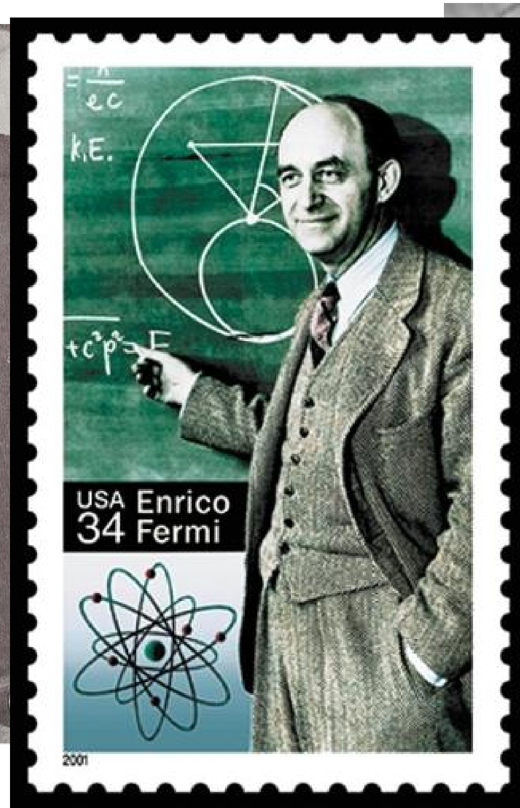





Numerical Statistical Mechanics

- Wood+Jacobsen → Monte Carlo
- Alder+Wainwright → Molecular Dynamics





Squares, Cubes, Disks, and Spheres (1950s-2009)

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Ruby Valley, Nevada, USA

1956: Zwanzig corrects Geilikmann's work

1961: Hoover & De Rocco correct Zwanzig's

1972: Frisch & Carlier find van der Waals

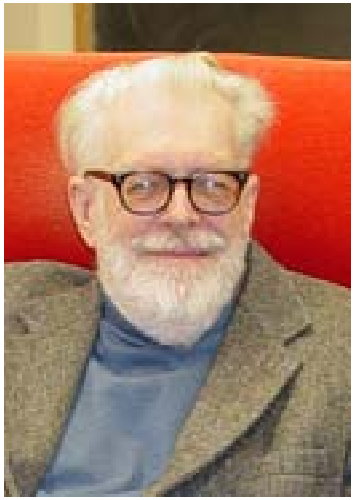
1972: Ree & Ree do not find van der Waals

1987: Woodcock studies percolation

2005: Clisby & McCoy generate B_8 - B_{10}

2009: Present Work (Single Speed MD)

1956 → Zwanzig's Idea



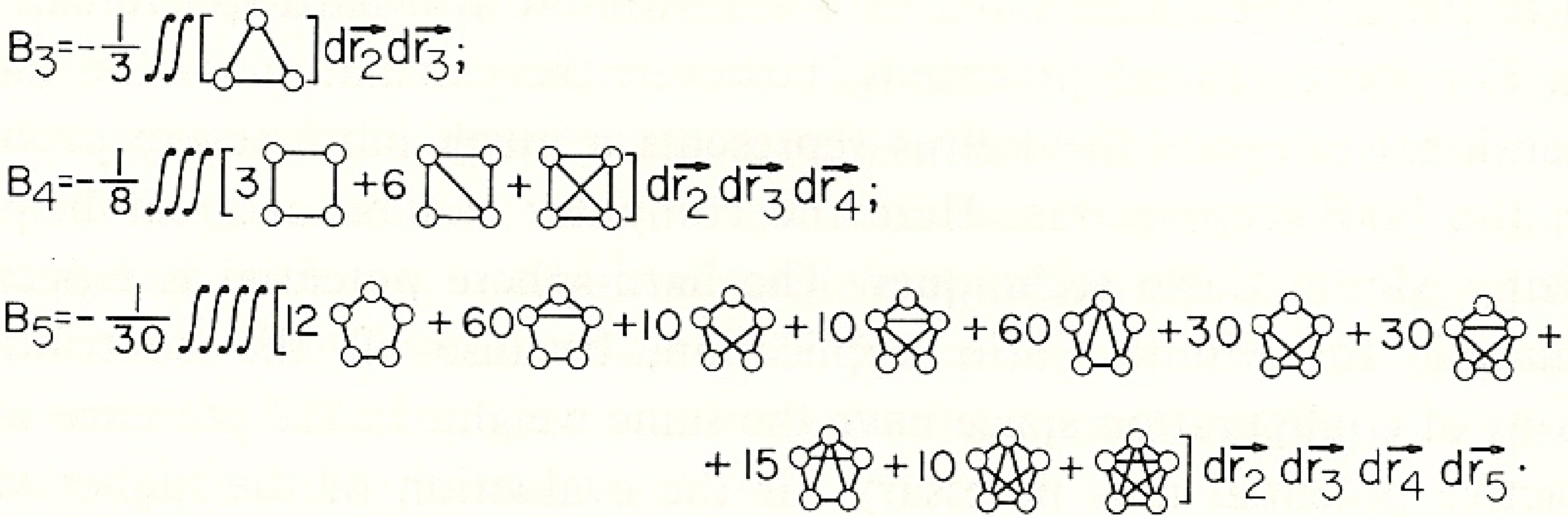
Use parallel hard cubes (or squares) to bound the properties of spheres (or disks).

$PV/NkT = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + B_5\rho^4 + \ldots$

Where PV/NkT comes from $\partial \ln Q_N / \partial \ln V$

Mayers' Recipe → B_2, B_3, B_4 … B_N

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



Ford & Uhlenbeck Catalog the Mayers' Diagrams through B_7

B_4 requires 3 integrals

B_5 requires 10 integrals

B_6 requires 56 integrals

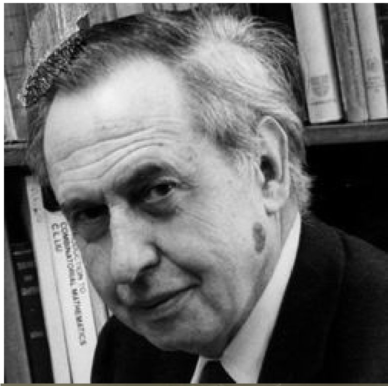
B_7 requires 468 integrals

. . .

B_N requires $2^{N(N-1)/2}/N!$

The integrals involve products of the Mayers' f-functions,

$$f = e^{-\phi/kT} - 1$$



Evaluation is **Easy** for Cubes

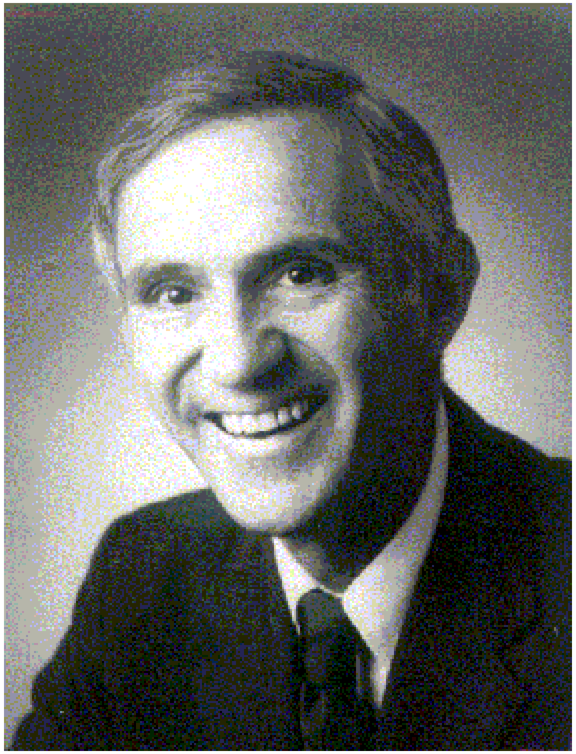
Hoover & De Rocco calculated integrals:

Both B_6 and B_7 are Negative for Cubes!

$$PV/NkT = 1 + 4\rho + 9\rho^2 + 11.333\rho^3 + 3.160\rho^4 - 18.880\rho^5 - 43.503\rho^6$$

$$\approx \frac{[1+1.459\rho+2.288\rho^2+0.915\rho^3]}{[1-2.541\rho+3.450\rho^2-1.355\rho^3]}$$

[B_7 requires 468 integrals.]



Evaluation is Harder for Spheres

Both B_6 and B_7 are Positive for Spheres!

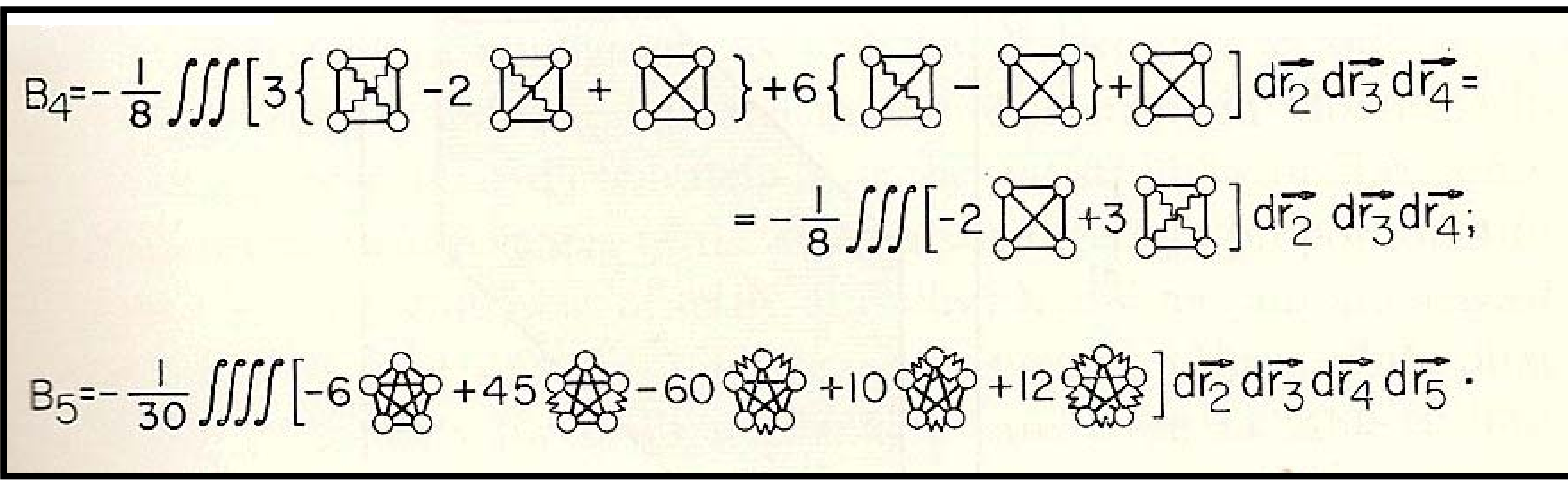
(Zwanzig's Idea was wrong.)

Ree and Hoover's Simplification:

$$1 = e^{-\phi/kT} - (e^{-\phi/kT} - 1)$$

Made it possible to Compute B_{10}!

Number of Integrals Somewhat Reduced
and
Numerical Cancellation Greatly Reduced



2006: Clisby/McCoy → $B_8 – B_{10}$

Number of Integrals is now quite large:

B_{10} requires 4,980,756 Monte Carlo integrals! [Instead of 9,743,542].

The Mayers' series appears to converge throughout the fluid phase with no convincing evidence for negative B_N for either hard disks or hard cubes and no sweeping generalizations.

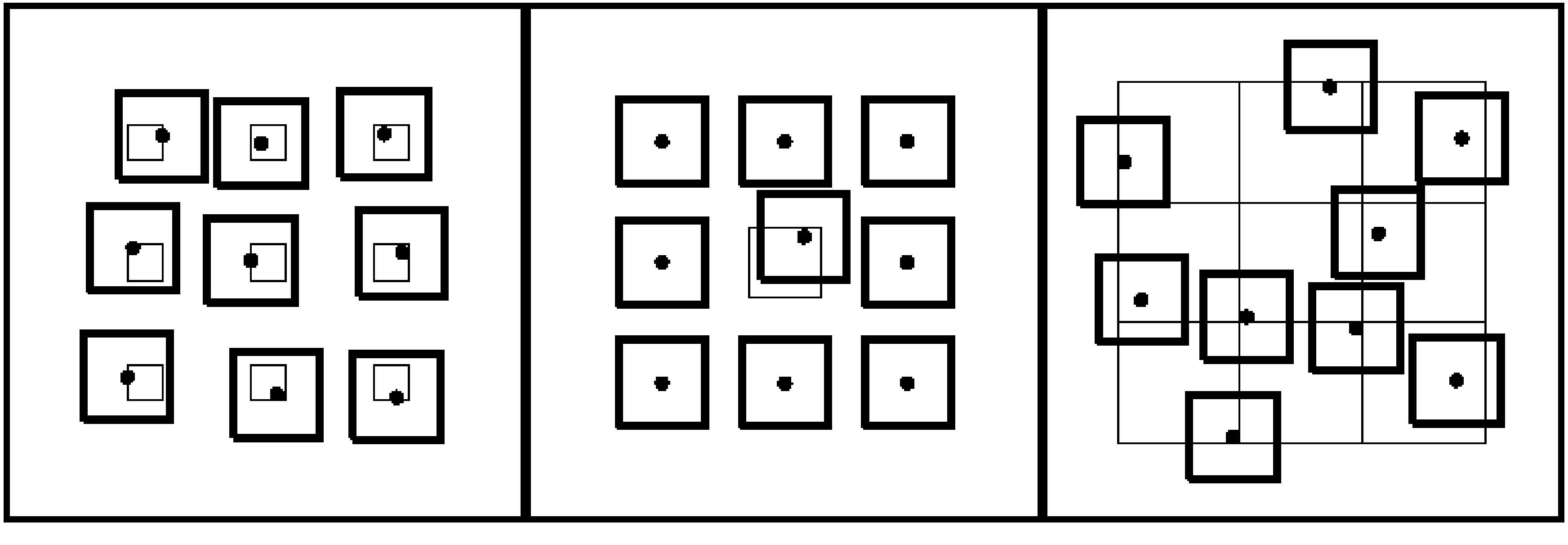
Free Volume & Cell Theories

- Because configurational properties are independent of mass why not look at a single very light “Wanderer” particle?
- Such a particle traces out a “Free Volume” in the “Cell” formed by its neighbors.

$$a_f \approx [(A/N)^{1/2} - 1]^2$$

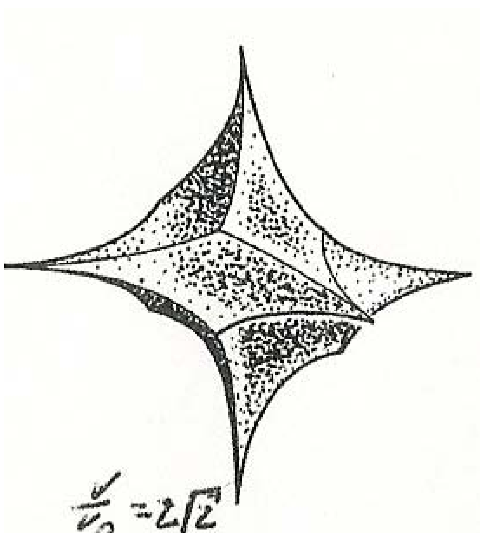
$$v_f \approx [(V/N)^{1/3} - 1]^3$$

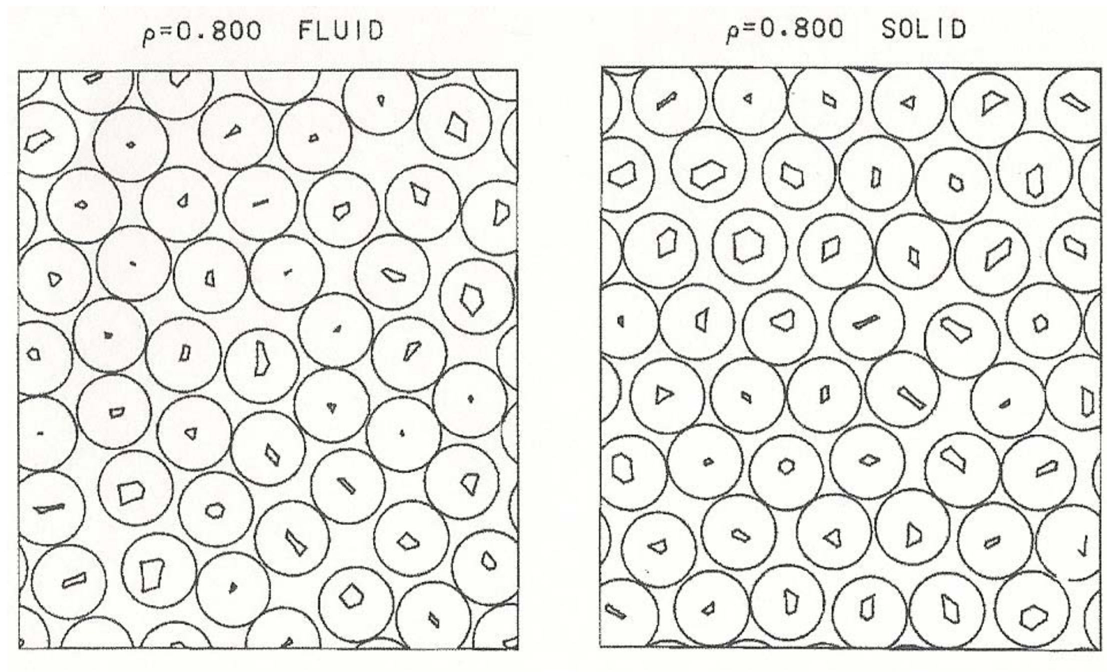
Three Useful Cell-Model Types:



Consistent, Inconsistent, Single-Occupancy

What do Free Volumes Look Like?





Hard Spheres
J. Chem. Phys. (1951)

Hard Disks
J. Chem. Phys. (1979)

Free-Volume Equation of State

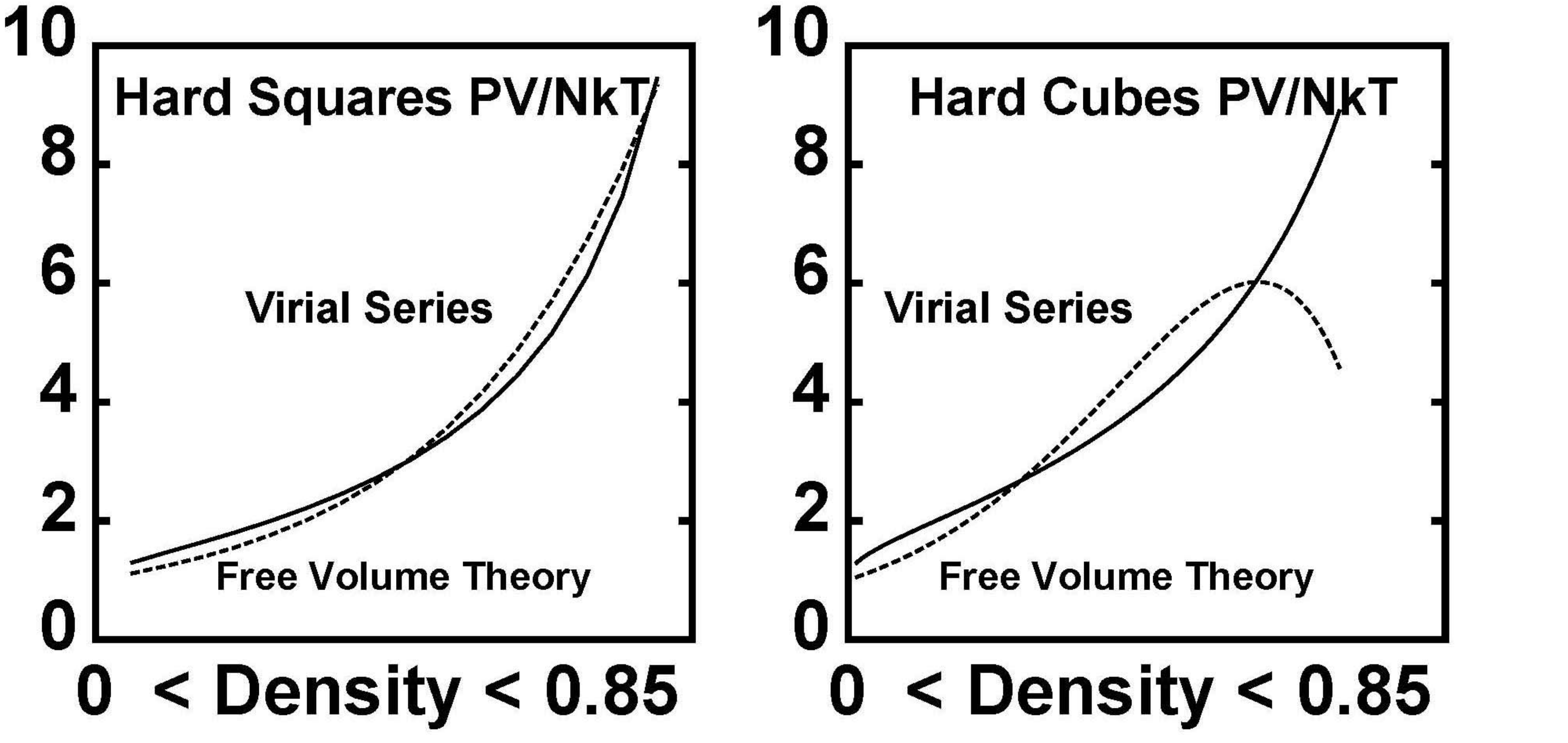
$PV/NkT = \partial \ln v_f / \partial \ln V = 1/[1 - \rho^{1/D}]$ where D is the dimensionality of the system.

This form follows from bounds on Q_N.

Notice v_f is larger for solids than fluids!

v_f has a percolation transition (extensive to intensive at the percolation density).

Two Theoretical Approaches to Pressure



Simplified Molecular Dynamics suggested by factorization of Q_N

Does Ergodicity Require Chaos, Mixing?

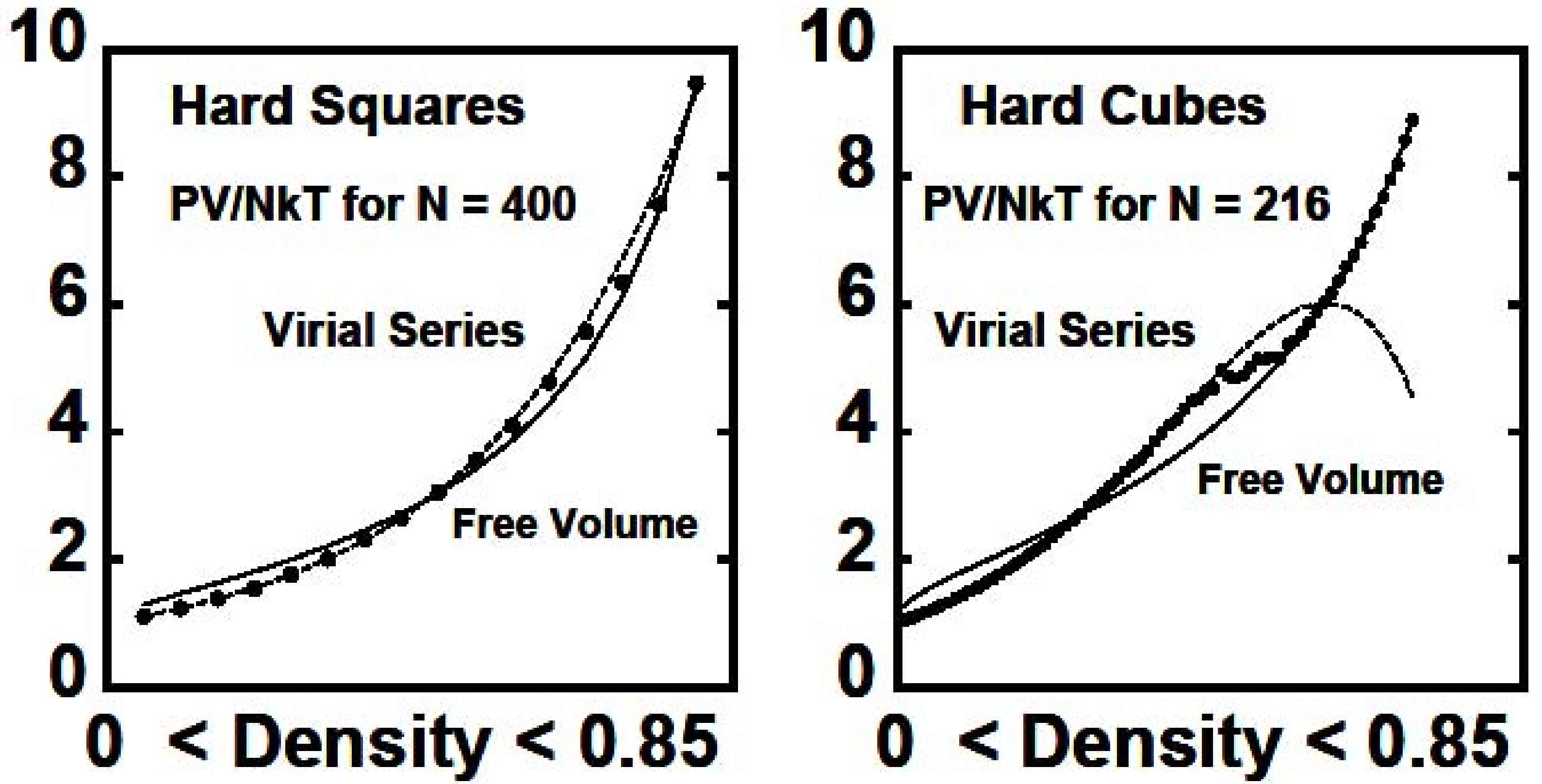
Are Hard Squares/Cubes Lyapunov Unstable?

Pressure from Single-Speed Molecular Dynamics agrees well with pressure from Maxwell-Boltzmann Dynamics.

$$v = \{ \pm 1, \pm 1, \pm 1 \}$$

Perfect agreement with Woodcock (1987)

Single Speed Molecular Dynamics



Hard Cube Pressure from Collision Rate

$$PV/NkT = 1 + B_2\rho(\Gamma/\Gamma_0)$$

$$= 1 + \Sigma < r \cdot F >/DNkT$$

Compute Γ_0 the Hard Way:

Relative speeds of $4^{1/2}$ or $8^{1/2}$ or $12^{1/2}$ with complicated cross-sections

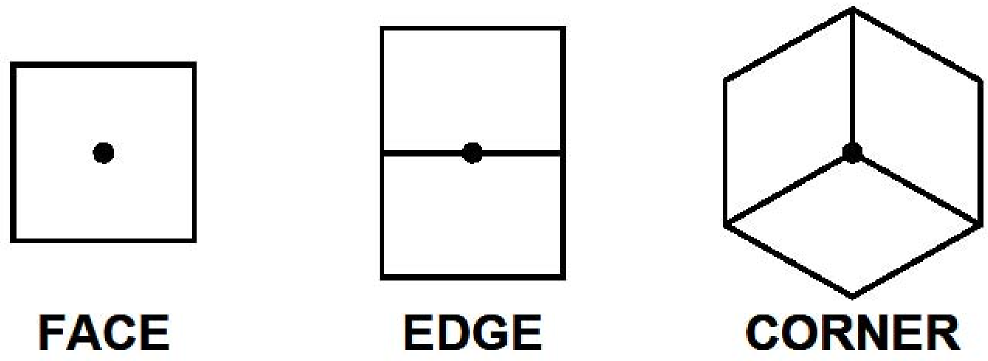
Compute Γ_0 the Easy Way:

Relative velocity of -2 with simple cross-sections (same result, of course!)

Simple versus Complicated

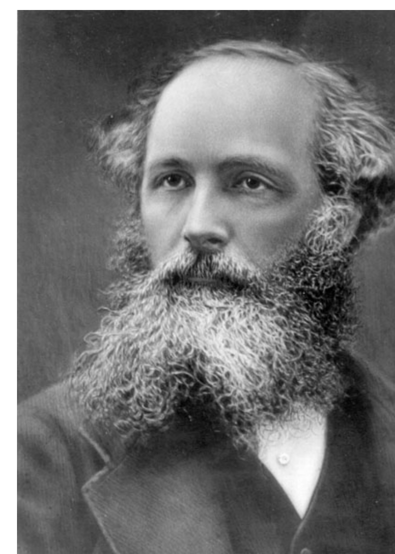
Cube Cross Sections the Hard Way

The Easy Way:
Add Face Contributions,
x + y + z

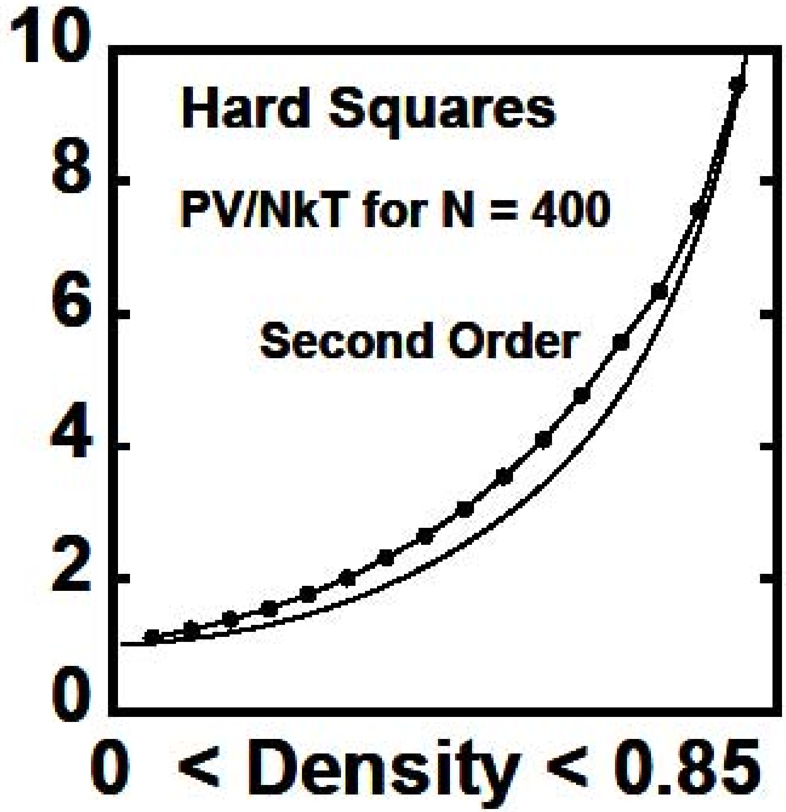


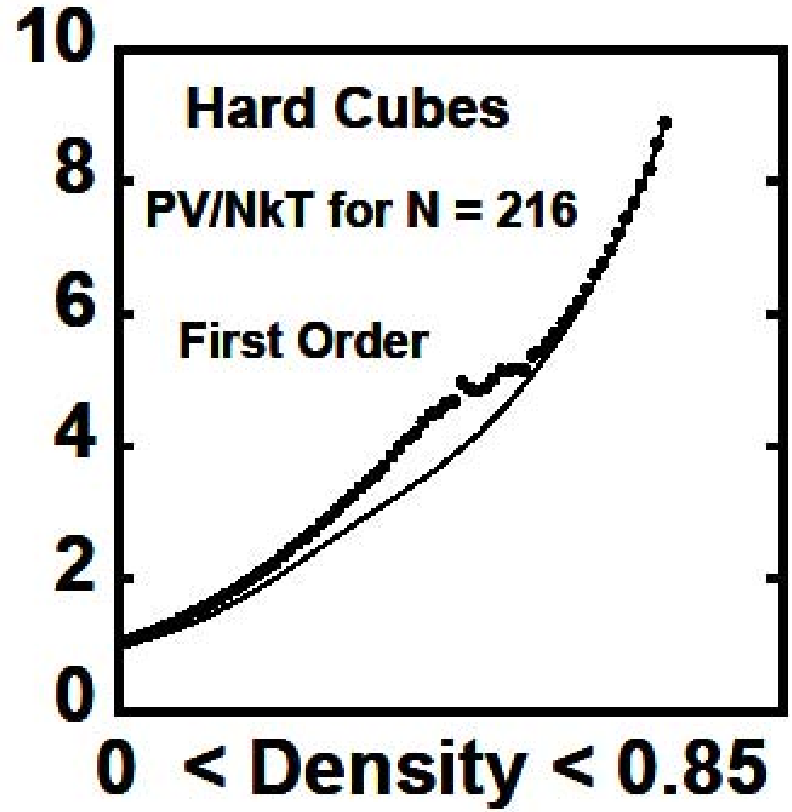
Pressure from Collision Rate

Hard Parallel Cubes make a good thermometer!



Fluid and Solid Molecular Dynamics



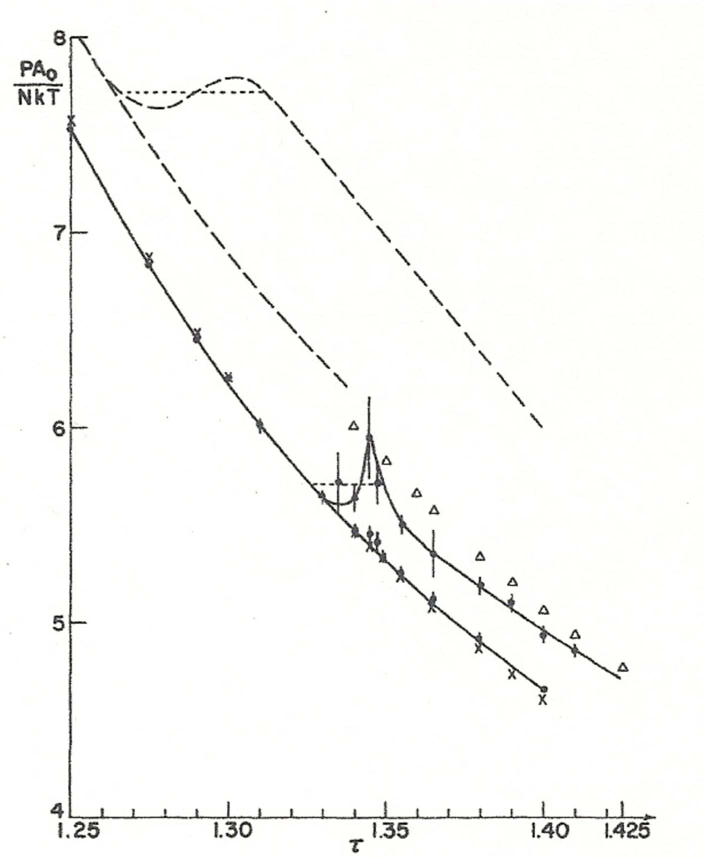


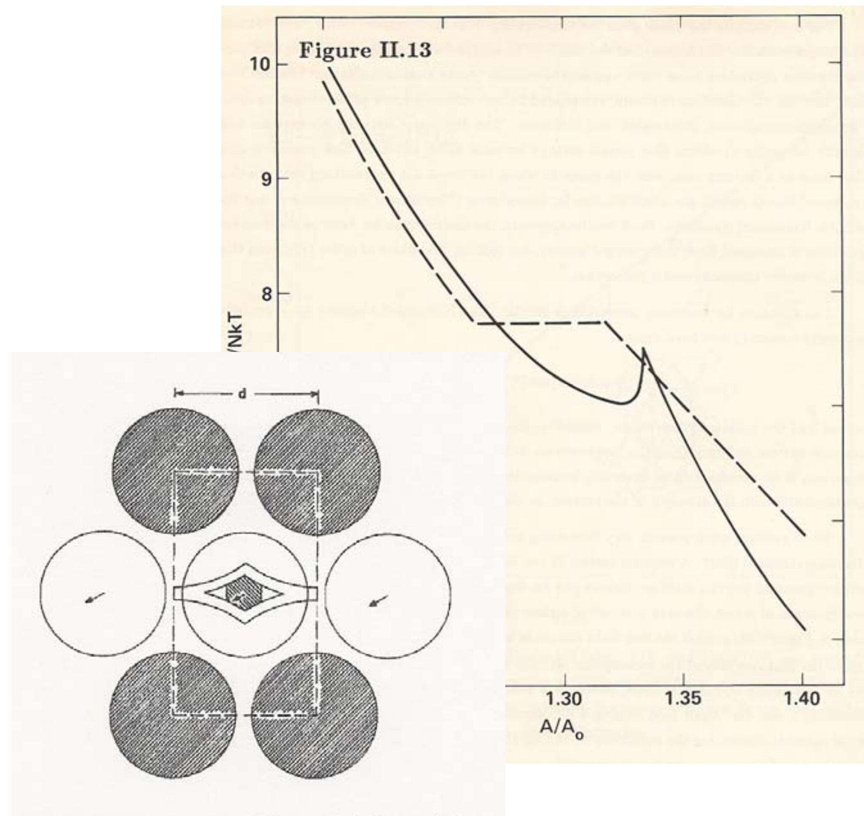
Mayer's Virial Series and the Free Volume Theory are good

But what about Wood's (and Frisch's) "Region of Confusion"???




Melting, van der Waals' Loops





Carlier & Frisch
400 Squares (1972)

Hoover, Alder, Wainwright
2 and 870 Disks (1963)

The Usual Melting Theories

Elastic Shear Constant Vanishes (Born)

Dislocations Proliferate (Kosterlitz)

Vibrational Amplitude Grows (Lindemann)

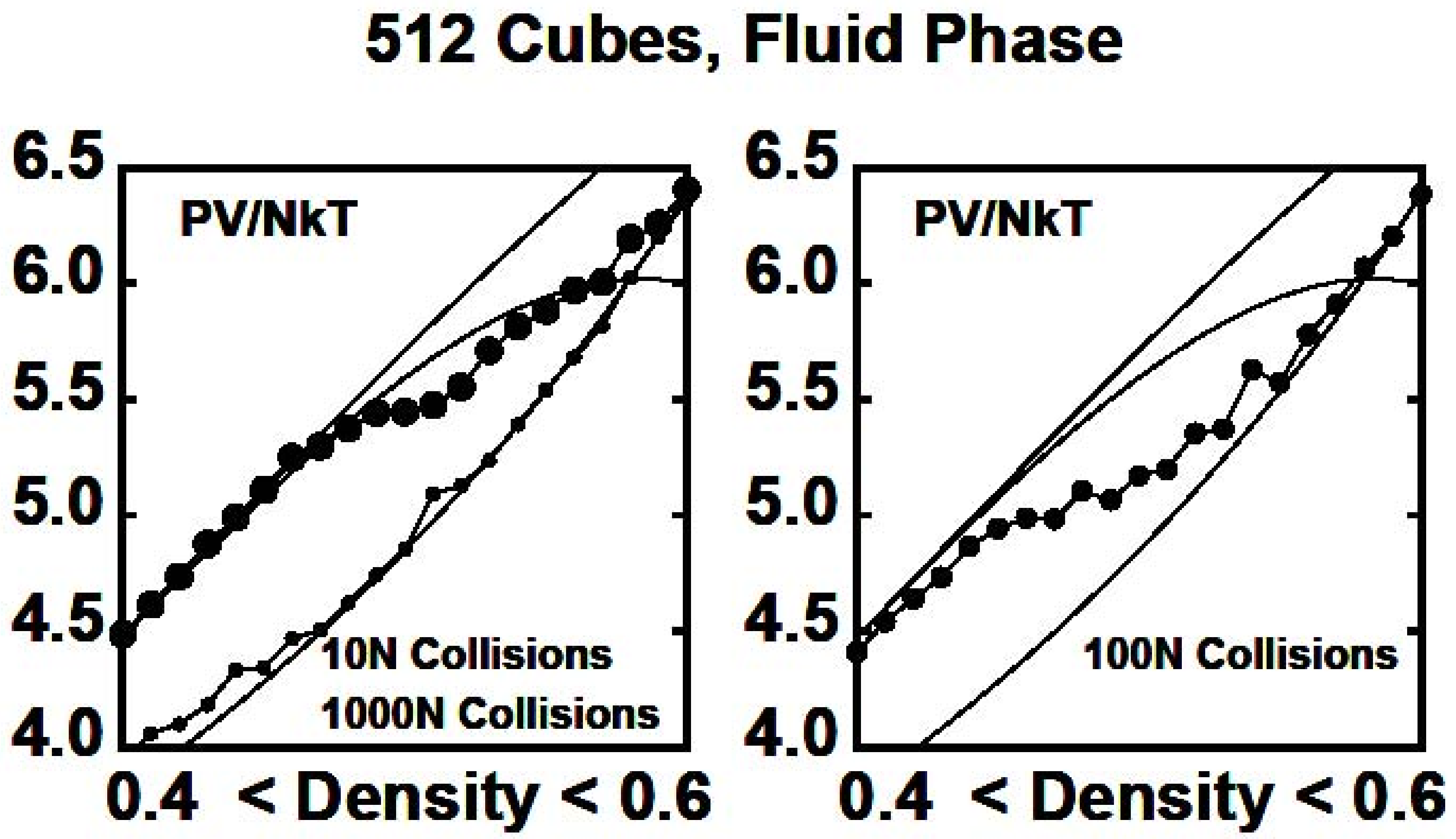
None of them is really foolproof.

Solution #1: Get More Data!

Solution #2: Use Kirkwood's

Single-Occupancy Entropy!

Solution #1: Get More Data

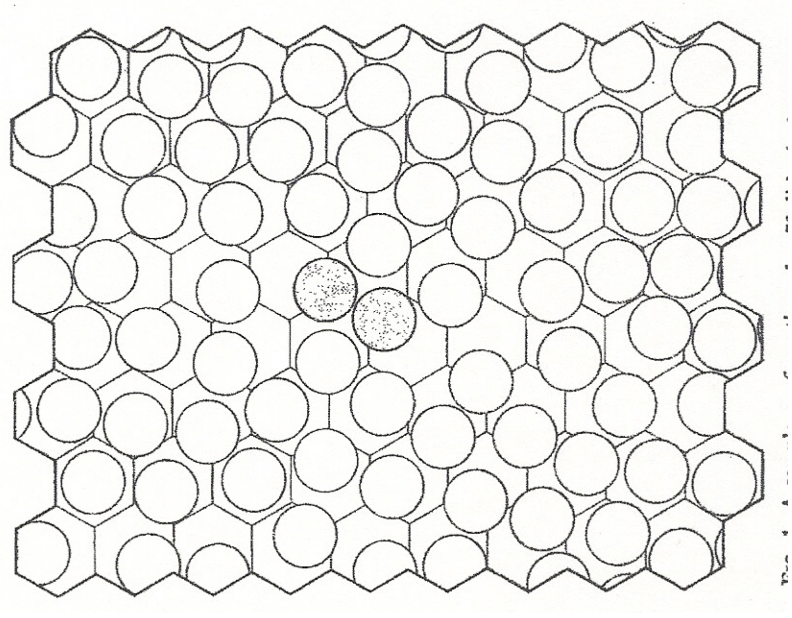


#2: Single Occupancy Dynamics

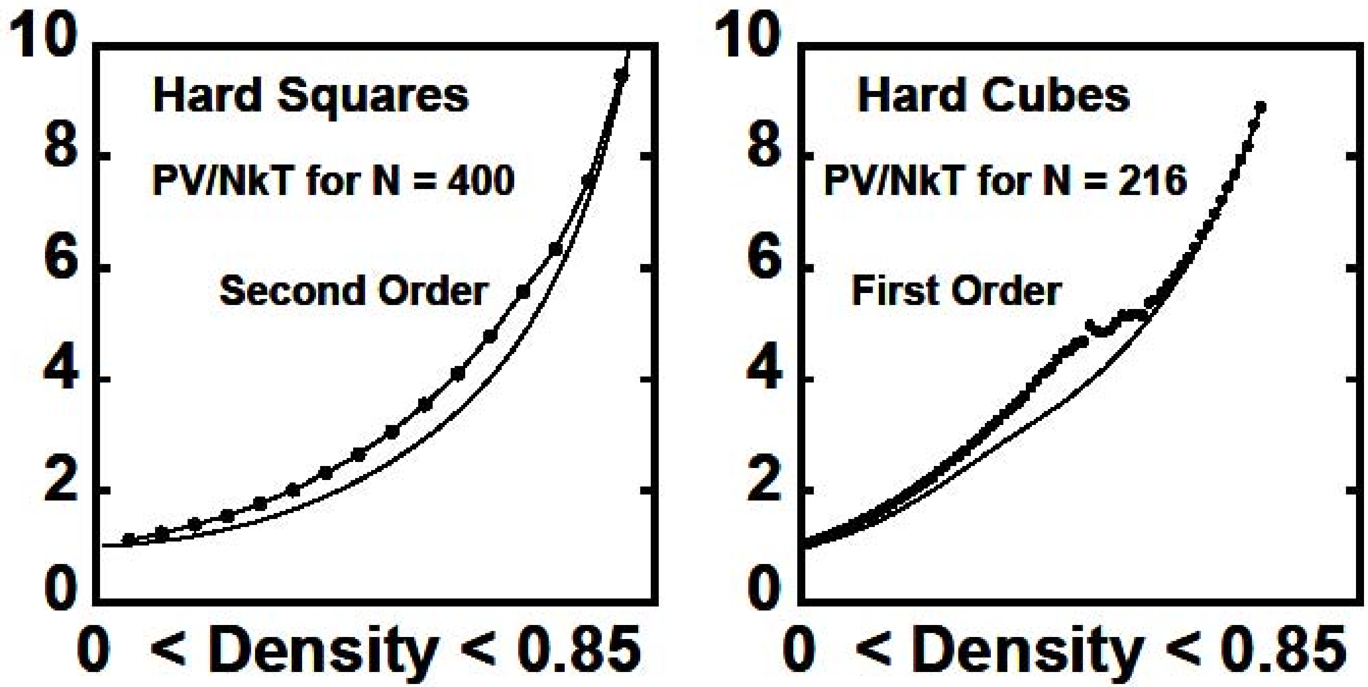
- **Particles occupy individual cells.**
- **Solid Phase goes Smoothly to $(V/N)^N$.**
- **Disks and Spheres (1967).**

$$G = E + PV - TS$$

$$\Delta S/Nk = -\int (PV/NkT)\, d\ln\rho$$



Fluid and Solid Molecular Dynamics



The difference in Areas is necessarily ΔS = NkT.

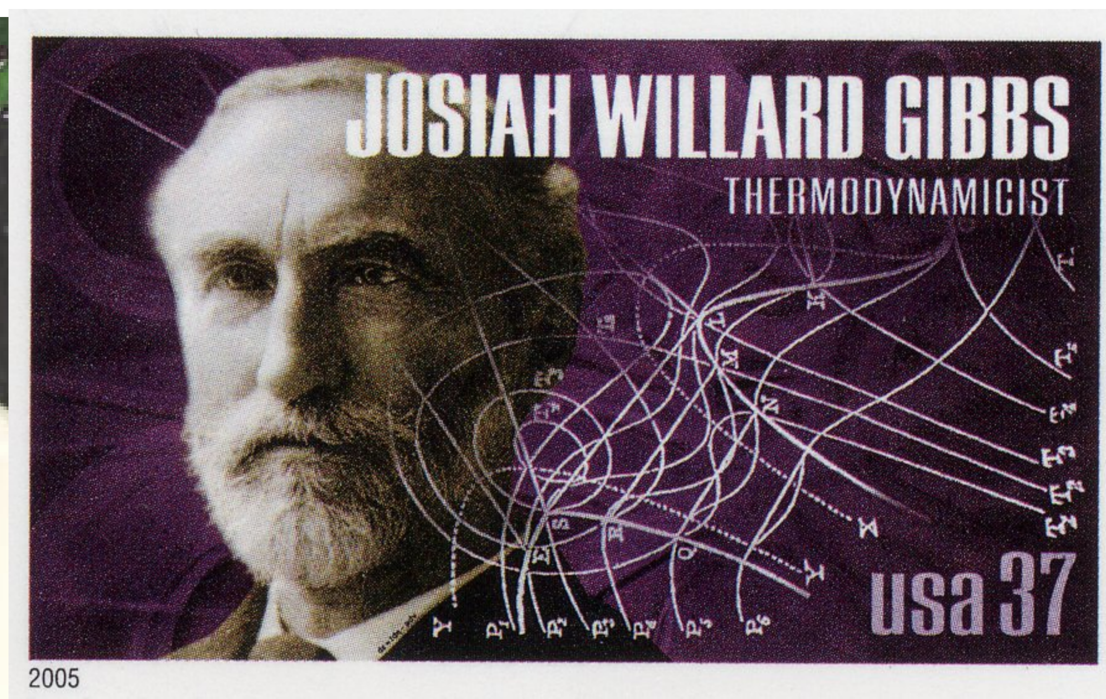
Lower Curves are Single-Speed Single-Occupancy Data

Single Occupancy Results

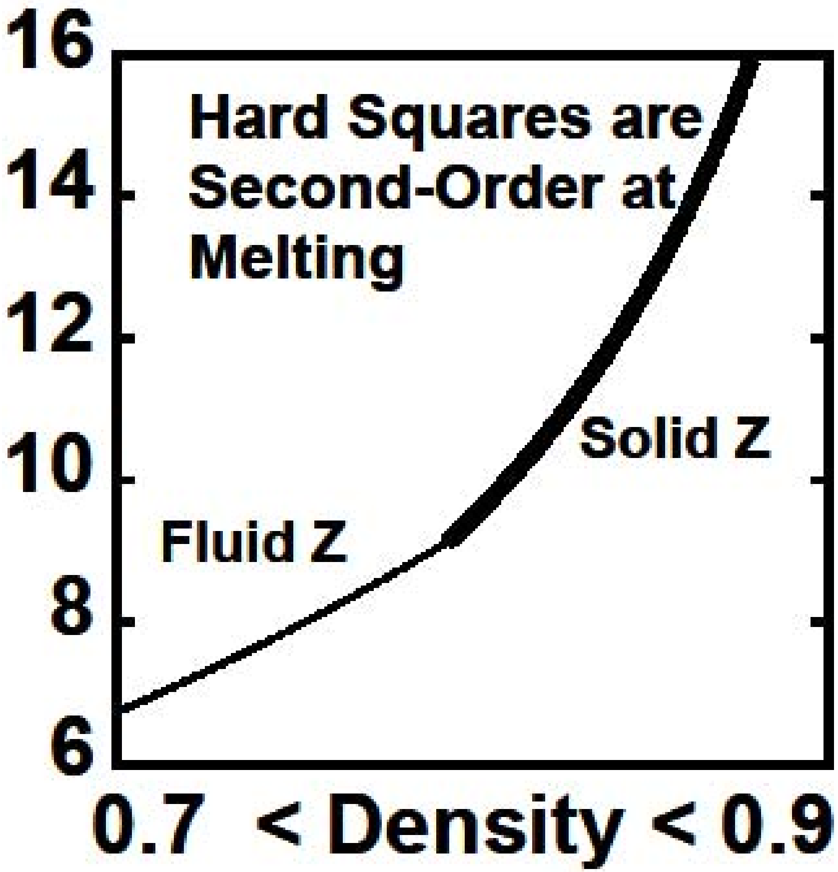
Squares have a Second-Order Transition.

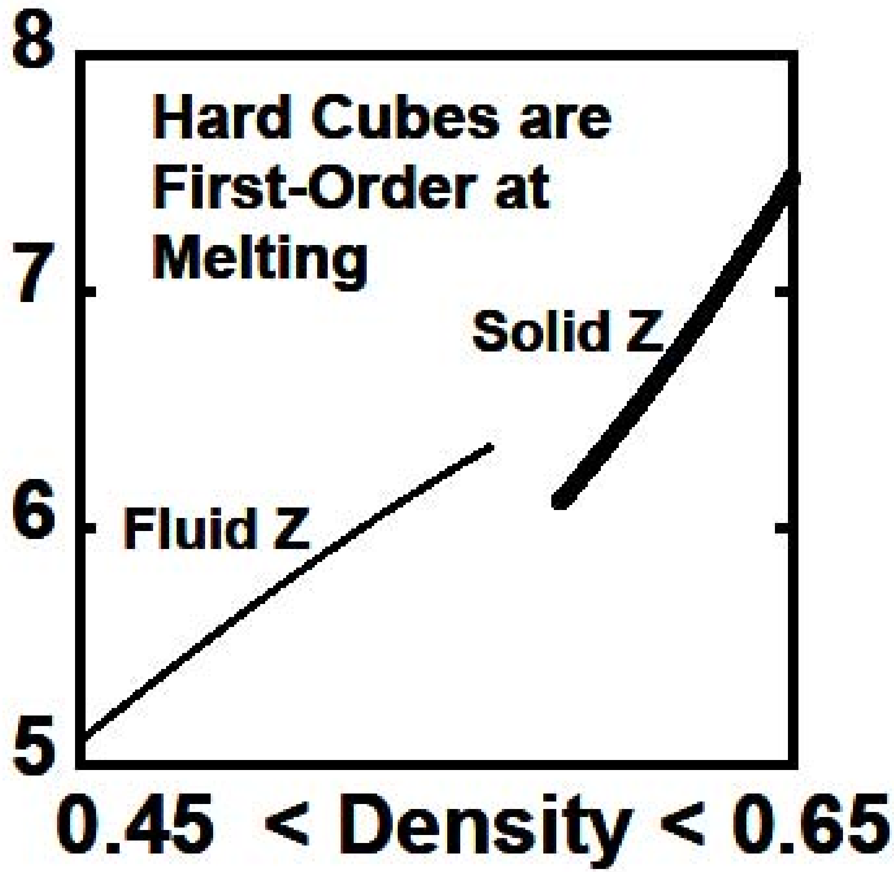
Cubes have a First-Order Transition.

Free Volume Theory is good for Solids.



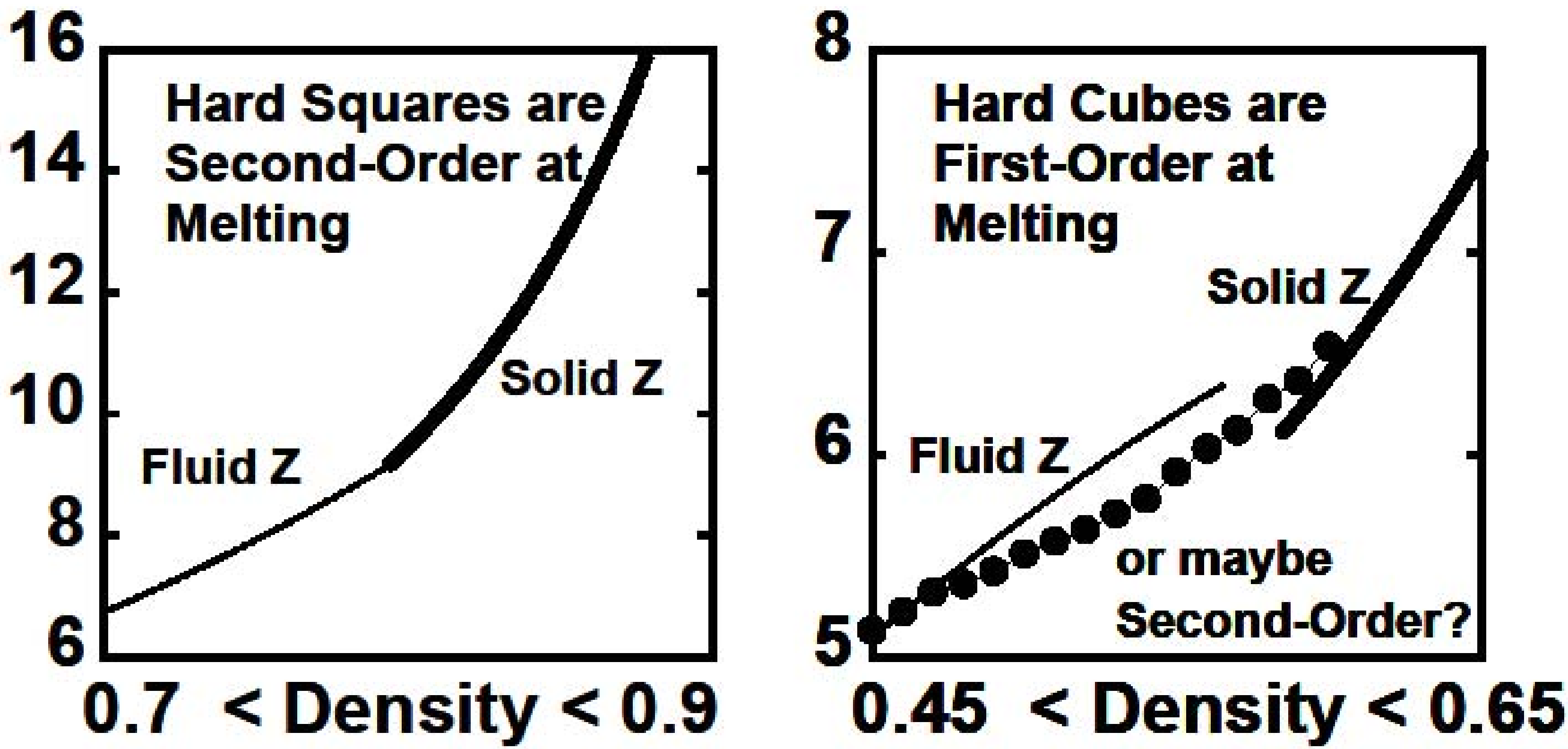
Conclusions from Our Work #1





Single Speed Dynamics Works!

Conclusions from Our Work #2



More Data are Always Handy!

Conclusions & Things to do

- Melting Transitions for Squares and Cubes resemble those of Disks and Spheres. Single Occupancy is good!
- Bifurcations and Lyapunov Instability should be investigated.
- B_8 through B_{10} should be calculated.
- Shear Stress for Cubes should be used to characterize the Solid Phase.