May 2009, Lecture #2
Statistical Mechanics:
Structure

TSTC Lectures:
Theoretical & Computational Chemistry

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$S = k_B \log W$

- Boltzmann's headstone at the Vienna Zentralfriedhof.

- Photo by Daderot on www.SklogWiki.org
- By the way, SklogWiki's symbol, $\Theta\Delta^{cs}$,is the short-hand used by James Clerk Maxwell for the word thermodynamics.

This Lecture

- Part II, continued:
  - Statistical Mechanics: Ideal
    - Cf. "Introduction to Modern Statistical Mechanics" by D. Chandler, (Oxford University Press, USA, 1987) —The green book ☺
    - Cf. "Statistical Mechanics" by B. Widom
    - Cf. "Basic concepts for simple and complex liquids" by J. L. Barrat & J- P. Hansen
- Part III:
  - Statistical Mechanics: Nonideal
    - Cf. Ibid!
- Part IV:
  - Statistical Mechanics of Liquids

Major Concepts, Part II — Ideal

- Thermodynamics (macroscopic theory)
  - *S*-conjugate variables
  - Legendre Transforms
- Statistical Mechanics—Fundamentals
  - Ensemble
  - Ensemble Averages & Observables
  - Partition Functions
  - Ergodicity
- Entropy and Probability
- Ensembles
  - Extensive vs. Intensive variables
- Harmonic Oscillator
- Ideal Gas

Sampling by:
- Monte Carlo
- Molecular Dynamics

Ensembles:
- (*S,V,N*) μcanonical
- (*T,V,N*) Canonical (or Gibbs)
- (*T,V,μ*) Grand-Canonical
- (*T,P,N*) Isothermal-Isobaric

Completing the Square

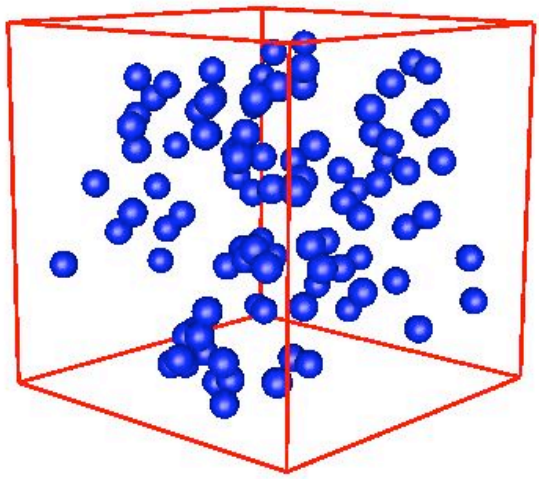
$$\int_{-\infty}^{+\infty} dx\, e^{-2\left(x-\frac{(a+b)}{2}\right)^2+\frac{1}{2}(a-b)^2} \quad = \quad e^{\frac{1}{2}(a-b)^2} \int_{-\infty}^{+\infty} dx\, e^{-2x^2}$$

$$\boxed{\int_{-\infty}^{+\infty} dx\, e^{(x-a)^2+(b-x)^2} \quad = \quad e^{\frac{1}{2}(a-b)^2} \sqrt{\frac{\pi}{2}}}$$

$$\begin{aligned}
(x-a)^2+(b-x)^2 &= \left(x^2-2ax+a^2\right)+\left(b^2-2bx+x^2\right) \\
&= 2x^2-2(a+b)x+a^2+b^2 \\
&= 2\left(x^2-(a+b)x\right)+a^2+b^2 \\
&= 2\left(x^2-(a+b)x+\frac{(a+b)^2}{4}\right)-\frac{(a+b)^2}{2}+a^2+b^2 \\
&= 2\left(x-\frac{(a+b)}{2}\right)^2-\frac{1}{2}\left(a^2+2ab+b^2\right)+a^2+b^2 \\
&= 2\left(x-\frac{(a+b)}{2}\right)^2+\frac{1}{2}\left(a^2-2ab+b^2\right) \\
&= 2\left(x-\frac{(a+b)}{2}\right)^2+\frac{1}{2}(a-b)^2
\end{aligned}$$

Gas

Consider N particles in volume, V



with a generic two-body potential:

$$V(\vec{r}_1,\ldots,\vec{r}_N) = \sum_{i<j} V_{ij}\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

and kinetic energy:

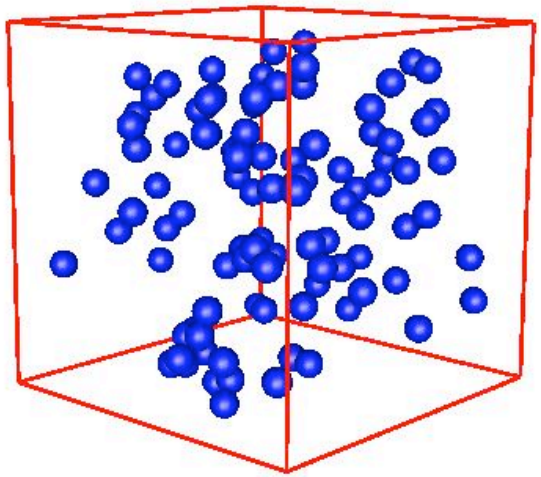
$$T(\vec{p}_1,\ldots,\vec{p}_N) = \sum_i \frac{\vec{p}_i^{\,2}}{2m_i}$$

The Canonical partition function:

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\vec{r} \int d\vec{p}\; e^{-\beta H(\vec{r},\vec{p})} \qquad d\vec{r} = dr_1 dr_2 \ldots dr_N$$

Integrating the K.E. Q in a Gas

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\vec{r} \int d\vec{p}\, e^{-\beta H(\vec{r},\vec{p})}$$



May generally be written as: (Warning: this is not separability!)

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\vec{p}\, e^{-\beta \sum_i^N \frac{p_i^2}{2m_i}} \int d\vec{r}\, e^{-\beta V(\vec{r})}$$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

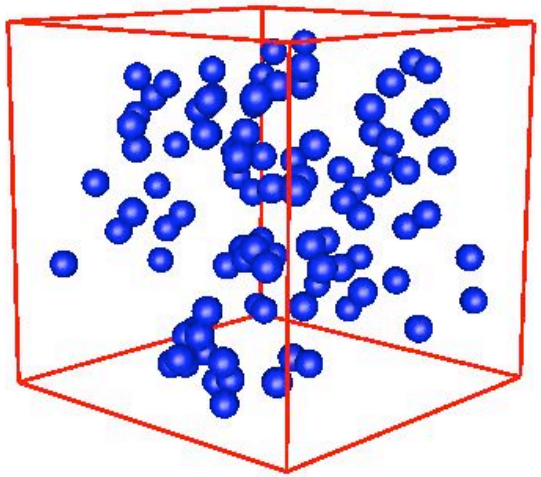
With the generic solution for *any* system

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \prod_i^N \left(\frac{2m_i\pi}{\beta}\right)^{3/2} \int d\vec{r}\, e^{-\beta V(\vec{r})}$$

No Interactions→Ideal Gas

Assume:

1. Ideal Gas → $V(r)=0$
2. Only one molecule type: $m_i=m$



$$\int d\vec{r}\, e^{-\beta V(\vec{r})} = \int d\vec{r} = V^N$$

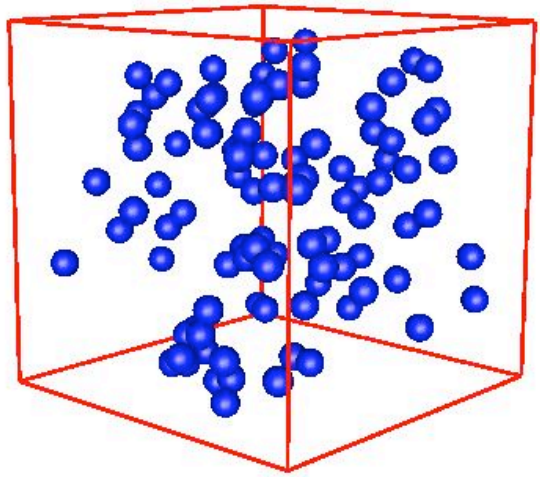
$$\prod_i^N \left(\frac{2m_i\pi}{\beta}\right)^{3/2} = \left(\frac{2m\pi}{\beta}\right)^{3N/2}$$

The ideal gas partition function:

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \left(\frac{2m\pi}{\beta}\right)^{3N/2} V^N$$

The Ideal Gas Law

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N} \left(\frac{2m\pi}{\beta}\right)^{3N/2} V^N$$



Recall:

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$$

$$A = -k_\mathrm{B}T\ln(Q)$$

The Pressure

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$P = k_\mathrm{B}T\frac{\partial \ln(Q)}{\partial V}$$

$$P = k_\mathrm{B}T\frac{N}{V}$$ Ideal Gas Law!

Ideal Gas: Other Observables

$$E(T,V,N) = -\frac{\partial \ln Q}{\partial \beta}$$

$$Q = \left(\frac{1}{2\pi\hbar}\right)^{3N}\left(\frac{2m\pi}{\beta}\right)^{3N/2} V^N$$

$$A(T,V,N) = -kT \ln Q$$

$$S(T,V,N) = \frac{E-A}{T} \qquad \text{Recall: } A = E - TS$$

$$\Delta(T,P,N) = \int_0^\infty e^{-\beta PV} Q(T,V,N)\,dV$$

$$G(T,p,N) = -kT \ln \Delta$$

$$S(T,p,N) = k \ln \Delta + kT\left(\frac{\partial \ln \Delta}{\partial T}\right)_{N,P}$$

Major Concepts, Part III

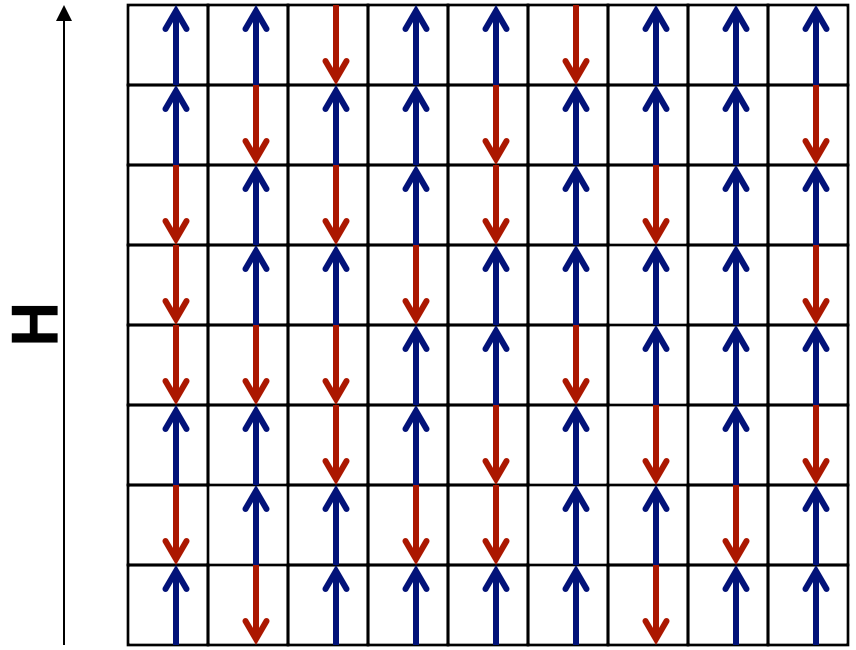
- **Non-Ideal Systems**
- Ising Model
  - *H*: Applied Field
  - *J*: Interaction (non-ideality)
  - Isomorphic to Lattice Gas!
  - Geometric vs. Energetic Frustration
- Phase Transitions
  - Spontaneous magnetization & Critical Temperature
  - Exact solution for *J*=0 (ideal)
  - Nonzero *J* Ising Solution in 1D (exact, transfer matrix)
  - Nonzero *J* Ising Solution in 2D (exact, Onsager)
- Mean Field Theory (Approximate)
- Monte Carlo (Numerical)

Non-Ideal Systems

- **Ideal systems≡non-interacting systems**
  - **i.e. ideal gas**
- **Non-ideal systems≡Most systems**
  - **Interactions between particles**
  - **One manifestation of particle interactions is the possibility of phase transitions**
  - **E.g., Spin Ising System or Lattice Gas:**
    - **Interactions included only at "nearest neighbors"**

Ising Spin (Magnet) Model

- **Ising model is lattice of spins.**
  - **Each square is large enough to hold one spin.**
- ***H*: magnetic field**
- **μ: magnetic moment**
- **S_i: direction of spin (±1)**
- **Isomorphic to lattice gas**



$$E_\nu(\{S_i\}) = -\sum_{i=1}^{N} H\mu S_i + \text{interaction energy}$$

Ideal Ising Model: *Q*

- **What if the interaction energy term is 0 (i.e. the system is ideal)?**
  - **the partition function can then be obtained readily:**

$$Q(\beta) = \sum_{\{S_i\}} e^{-\beta \sum_{i=1}^{N} H\mu S_i}$$

$$= \prod_{i=1}^{N} \sum_{S_i=\pm 1} e^{-\beta H\mu S_i}$$

$$= (e^{-\beta H\mu} + e^{\beta H\mu})^N = (2\cosh(\beta H\mu))^N$$

- **Using the partition function many observables can be calculated.**

Ideal Ising Model: <*E*>

- **The average energy of the system is given by:**

$$Q(\beta) = (2\cosh(\beta H\mu))^N$$

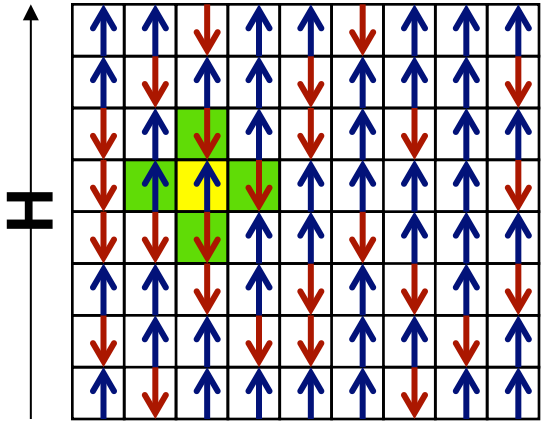
$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$= -NH\mu \frac{\sinh(\beta H\mu)}{\cosh(\beta H\mu)} = -NH\mu \tanh(\beta H\mu)$$

Interactions in the Ising Model

- **In the Ising model, only nearest neighbors interact.**

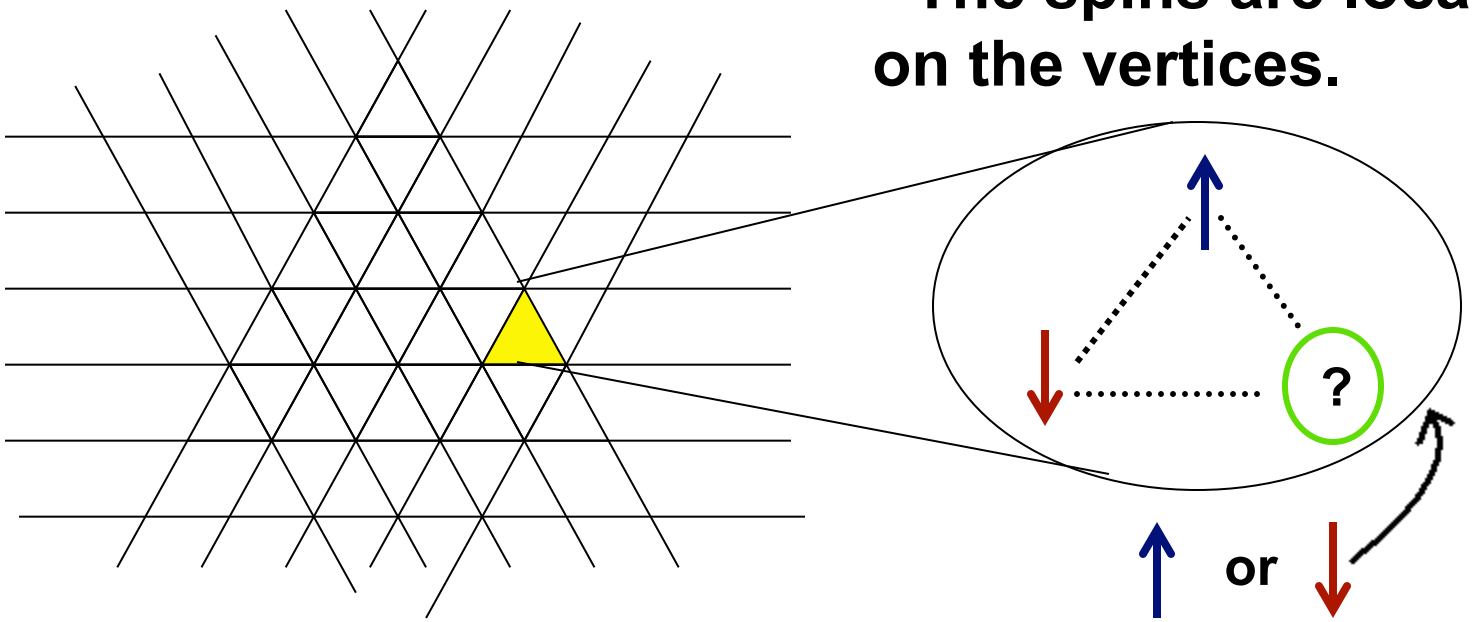
$$-J\sum_{ij}{}' s_i s_j$$



  - ***J*** **is the coupling constant**
  - **Why not add terms with s_i squared or higher power?**
- ***J*** **> 0 (ferromagnet)**
  - **energetically favorable for spins to be aligned**
- ***J*** **< 0 (antiferromagnet)**

Frustration

• **Frustration occurs when you can't avoid unfavorable contacts. E.g, in a non-rectilinear Ising model:**



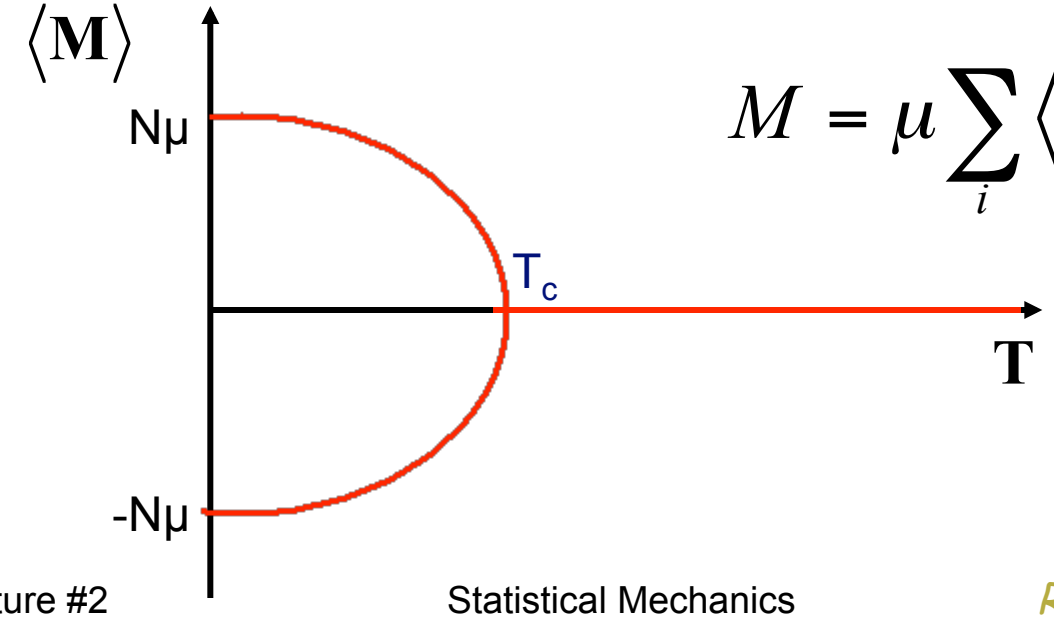
• **The spins are located on the vertices.**

• **J < 0 Antiferromagnetic system**

• **Frustration arises from unfavorable contacts**

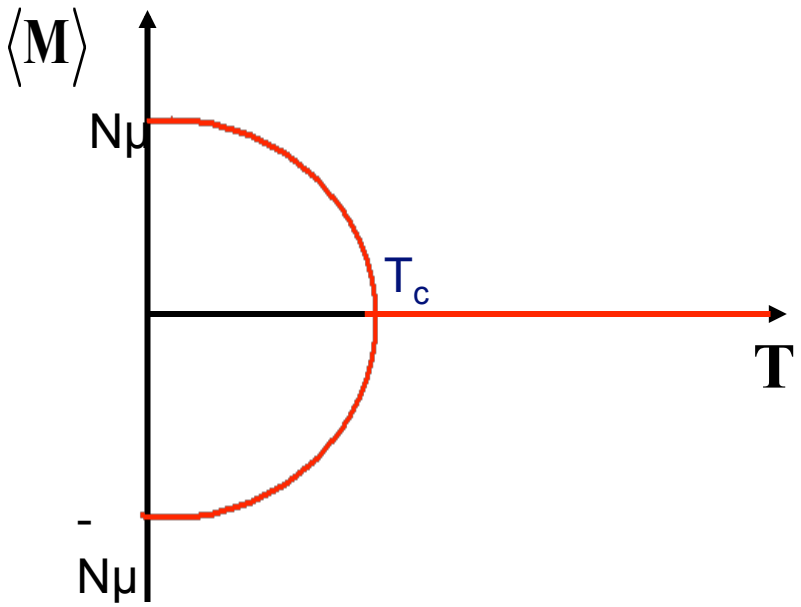
Phase Transitions in Ising?

- **Through nearest neighbor interactions, spins separated by a macroscopic distance can influence each other.**
- **Long range correlations lead to long range order**
  - **For the spin Ising system, *long range order* is indicated by net magnetization of the system even in the absence of a magnetic field.**



$$M = \mu \sum_i \langle S_i \rangle = N\mu \langle S \rangle$$

Phase Transitions in Ising?



$$M = \mu \sum_i \langle S_i \rangle = N\mu \langle S \rangle$$

- **Order-disorder (phase) transition occurs at T_c**
- **Does a phase transition exist?**
  - **Does a region with net magnetization exist?**
- **If H=0 when J>0 and there is a region of net magnetization then the system shows spontaneous magnetization.**

PMF: *F(M)*

- The potential of mean force (PMF) gives rise to a free energy in the net magnetization
- At $T>T_c$
  - *F(M)* is a single well centered at *M*=0
- At $T=T_c$
  - *F(M)* is a single well centered at *M*=0, but the second derivative at 0 is 0
- At $T<T_c$
  - *F(M)* is a double well with a saddle at *M*=0, and now giving rise to TWO stable nonzero M's.

1D Ising Model: Find T_c

- **How can the critical temperature, T_c, be found?**
  - Calculate the partition function for the system Q(β,H)

$$\langle M \rangle = \left(\frac{\partial(\ln Q)}{\partial(\beta H)} \right)_{H=0} \left[\propto \sinh(\beta \mu H) \ \text{ in 1D} \right]$$

  - If $|\langle M \rangle| > 0$ for any β then the system exhibits spontaneous magnetization (an order-disorder transition).
  - Peierl's Theorem argues that there is no net magnetization in 1D.
  - It also claims that if you have net magnetization at a given *T* for nD, then you have net magnetization at that same *T* at all higher dimensionality

1D Ising Model: Find Q(β,H)

$$Q(\beta,H)=\sum_{\{S_i\}}\exp\left[\beta\mu H\sum_i S_i+\beta J\sum_{i,j}{}' S_iS_j\right]=\sum_{\{S_i\}}\exp\left[\beta\mu H\sum_i\frac{S_i+S_{i+1}}{2}+\beta J\sum_i S_iS_{i+1}\right]$$

$$=\sum_{\{S_i\}}\prod_i\exp[\beta\mu H\frac{S_i+S_{i+1}}{2}+\beta JS_iS_{i+1}]$$

$$=\sum_{\{S_i\}}\prod_i q_{S_iS_{i+1}}\qquad ;q=\begin{pmatrix} q_{1,1} & q_{1,-1}\\ q_{-1,1} & q_{-1,-1}\end{pmatrix}$$

Transfer Matrix

$$=Tr(q^N)=\lambda_+^N+\lambda_-^N\approx\lambda_+^N$$

$$=\exp\{N[\beta J+\ln\{\cosh(\beta\mu H)+[\sinh^2(\beta\mu H)+e^{-4\beta J}]^{1/2}\}]\}$$

Two Dimensions and Higher

- **Exact (analytic) result obtained by Lars Onsager in the 1940's using a 2D transfer matrix technique,**

$$T_C = 2.269\, J/k_B$$

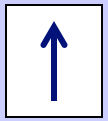
$$M \propto (T_C - T)^{\frac{1}{2}} \qquad \text{for } T < T_C$$

- **Peierl's Theorem guarantees $T_c > 0$ for the 3D and higher dimensionality Ising models**

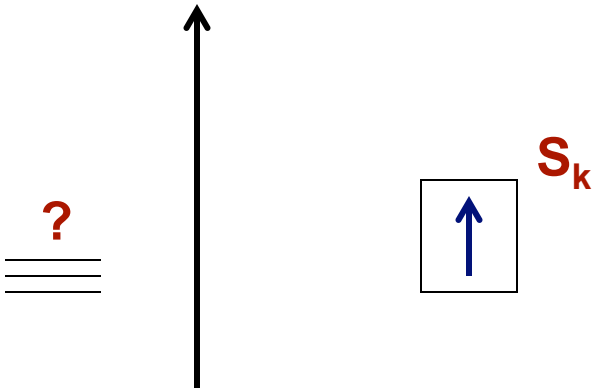
$T_c/(J/k_B)$	Numerical (Exact)	Onsager	Net Magnetization?
1D	0	0	*no*
2D	2.3	2.269	***yes***
3D	~4		*yes*
4D	~8		*yes*

Mean Field Theory (MFT)

Universe of spins



Tagged spin



H: Mean field due to the universe of spins

$$E_v(\{S_i\}) = -\sum_{i=1}^{N} H\mu S_i - \frac{J}{2}\sum_{i,j}{}' S_i S_j$$

$$\frac{\partial E}{\partial S_k} = -\mu H - J\left(\sum_j S_j\right)_k$$

$$\left\langle \frac{\partial E}{\partial S_k} \right\rangle = -\mu H - Jz\bar{S}$$

$z = 2D$

$\bar{S}$: Average spin of an equivalent neighbor

Mean Field Theory (MFT)

- **Consider a single spin system:** $E = S_k \cdot \left\langle \frac{\partial E}{\partial S_k} \right\rangle$

$$Q(\beta,1,H) = \sum_{S_{n=\pm 1}} \exp\{\beta(\mu H + Jz\bar{S})S_k\}$$

$$= 2\cosh\{\beta(\mu H + Jz\bar{S})\}$$

$$\langle S_k \rangle = \left(\frac{\partial \ln Q(\beta,1,H)}{\partial \beta \mu H} \right)_{H=0}$$

$$= \tanh(\beta Jz\bar{S})$$

- **But** $\bar{S} = \langle S_k \rangle$ **since no spin is special**
- **Obtain spontaneous magnetization at** $T_C = \frac{Jz}{k_B} = \frac{2DJ}{k_B}$

Variational MFT

- How do you know to choose the reference Hamiltonian to be that of an ideal system with mean forces?
- Gibbs-Bogoliubov-Feynman Inequality!

- Note also connections to:
  - perturbation theory
  - cumulant expansions
  - Mayer cluster expansion

Sping Ising Model: Summary

$T_c/(J/k_B)$	Numerical (Exact)	Onsager	MFT
1D	0	0	2
2D	2.3	2.269	4
3D	~4		6
4D	~8		8

- **MFT is not always accurate.**
  - •Accuracy increases with increasing dimensionality
  - •Flory-Huggins Theory is a MFT for polymers!
- **Sometimes need something better…**
  - • RG: Renormalization Group Theory

Monte Carlo: Naïve

Problem: $\int dx\, f(x)P(x) = ?,$ with $\mathrm{DIM}(x) \gg 1$

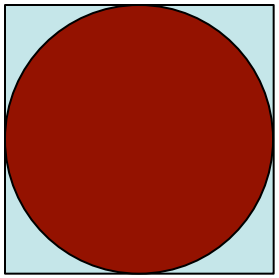
Ans. 1: Monte Carlo: Use random (uniform) sampling

Let $\{x_i\}$ be a "random" sequence of N numbers in the domain

$$\Rightarrow \boxed{\int dx\, f(x)P(x) \approx \frac{1}{N}\sum_{i=1}^{N} f(x_i)}$$

Naïve MC: Calculating π

$$\int dx\, f(x)P(x) \approx \frac{1}{N}\sum_{i=1}^{N} f(x_i)$$



Area of a square of sides with d:

$$A_{\rm sq} = d^2$$

Area of a disk of diameter, d:

$$A_{\rm circ} = \pi d^2/4$$

So the ratio of areas is:

$$\frac{A_{\rm circ}}{A_{\rm sq}} = \frac{\pi}{4}$$

Let $P(x)$ be a constant (viz., uniform in the square), and

$$f(x) = \begin{cases} 1 & \text{if } x \in \text{the disk} \\ 0 & \text{if } x \notin \text{the disk} \end{cases}$$

Let $\{x_i\}$ be a uniform sampling of the square, then

$$\pi \approx 4 \times \frac{1}{N} \times \sum_{i=1}^{N} f(x_i)$$

- Numerics of π:
  - $N_{\rm circ}$, $N_{\rm sq}$, $4*N_{\rm circ}/N_{\rm sq}$
  - 72 100 2.88 (1 digit)
  - 782 1000 3.128
  - 7910 10000 3.164 (2 digits)
  - 78520 100000 3.1408
  - 785322 1000000 3.141288 (3 digits)
  - 7854199 10000000 3.1416796
  - 78540520 100000000 3.1416208 (4 digits)
  - 785395951 1000000000 3.1415838
  - 1686652227 2147483647 3.14163459
  - …, …, 3.1415927 (8 digits)

Monte Carlo: Metropolis

- N. Metropolis, A. Rosenbluth, M.Rosenbluth, A. Teller and E. Teller, J. Chem. Phys. 21, 1087 (1953)

Problem: $\int dx\, f(x)P(x) = ?,$ with $\mathrm{DIM}(x) \gg 1$

Ans. 2: (Metropolis) Use a Markov Walk

Detailed Balance: $P(x)W(x \to x') = P(x')W(x' \to x)$
where W :: Transition Probability

$$\Rightarrow \boxed{W(x \to x') = \mathrm{MIN}\left[1, \frac{P(x')}{P(x)}\right]} = \mathrm{MIN}\left[1, e^{-\beta \Delta E_{x' \to x}}\right]$$

A Metropolis Monte Carlo step from x_i to x_{i+1} consists of N' move attempts with each accepted or rejected according the probability criteria relative to a random numer

The sequence $\{x_i\}$ consists of an initially equilibrated state, x_1, "propagated" for $N-1$ steps.

$$\Rightarrow \boxed{\int dx\, f(x)P(x) \approx \frac{1}{N}\sum_{i=1}^{N} f(x_i)}$$

Monte Carlo: Umbrella Sampling

Problem: $\int dx\, f(x)P(x) = ?,$ with $\mathrm{DIM}(x) \gg 1$

Ans. 3: (Importance Sampling) Use Loaded Dice!

$$\text{Suppose} \begin{cases} \cdot P(x) = P_0(x)P_1(x) \\ \cdot W(x \to x') = W_0(x \to x')W_1(x \to x') \end{cases}$$

$$\text{then } W_1(x \to x') = \mathrm{MIN}\left[1, \frac{W_0(x' \to x)P_0(x')P_1(x')}{W_0(x \to x')P_0(x)P_1(x)}\right]$$

So what? Choose x' using $P_0(x')$...

$$\Rightarrow \boxed{W_1(x \to x') = \mathrm{MIN}\left[1, \frac{P_1(x')}{P_1(x)}\right]}$$

The sequence $\{x_i\}$ consists of an initially equilibrated state, x_1, "propagated" for $N-1$ steps.

$$\Rightarrow \boxed{\int dx\, f(x)P(x) \approx \frac{1}{N}\sum_{i=1}^{N} f(x_i)}$$

Parallel Tempering & Replica Exchange

- Problem:
  - How do you sample all of the space on a corrugated energy landscape? (barriers greater than target T.)
- Answer:
  - run N many replicas using MC at N different temperatures, T_i, in parallel
  - Every so often, attempt exchanges between replicas according to

$$\text{probability} = \min(1, \exp([1/kT_i - 1/kT_j][E_i - E_j]))$$

  - Satisfies detailed balance

RH Swendsen and JS Wang, "Replica Monte Carlo simulation of spin glasses," *Phys. Rev. Lett.* **57**, 2607-2609 (1986)
C. J. Geyer, in Computing Science and Statistics Proceedings of the 23rd Symposium on the Interface, American Statistical Association, New York, 1991, p. 156.

Wang-Landau

- A Monte Carlo approach for obtaining the density of states, $\rho(E)$, directly
  - Rather than computing $g(r)$ or other observables
  - A random walk through energy space!
- Algorithm:
  - Initialize $\rho(E)$=1 for all E
  - Accept moves according to:
    - probability = min[1, $\rho(E_{\text{initial}})/\rho(E_{\text{trial move}})$]
    - Let E' be the energy of the state at the end of the trial
  - Update $\rho(E')= f\rho(E')$ & the histogram H(Set(E'))+=1
  - Stop once the histogram is "flat," [error in $\rho(E)$ = O{ln(f)}]
  - Iterate, now using smaller f,

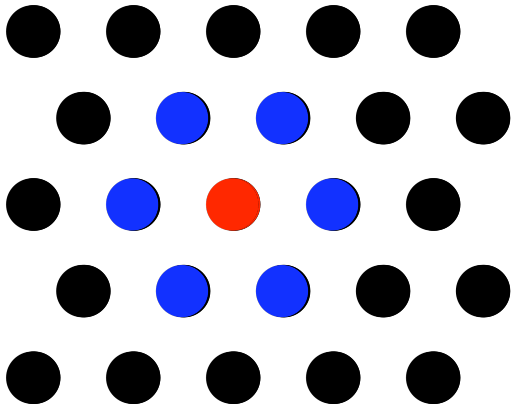
F. Wang & D.P. Landau, *Phys. Rev. Lett*. **86**, 205 (2001). [original version for spin Hamiltonian]

Major Concepts, Part IV

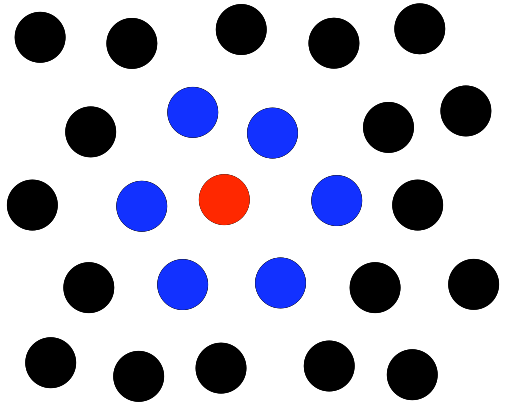
- Review:
  - Fluid Structure
    - Gas, liquid, solid, …
    - Radial distribution function, $g(r)$
  - Potential of Mean Force
  - Classical Determination of $g(r)$:
    - Integral Equation Theories
    - Molecular Dynamics
    - Monte Carlo
    - Scattering experiments (e.g., x-ray, or SANS)
- Renormalization Group Theory

Quantifying Structure

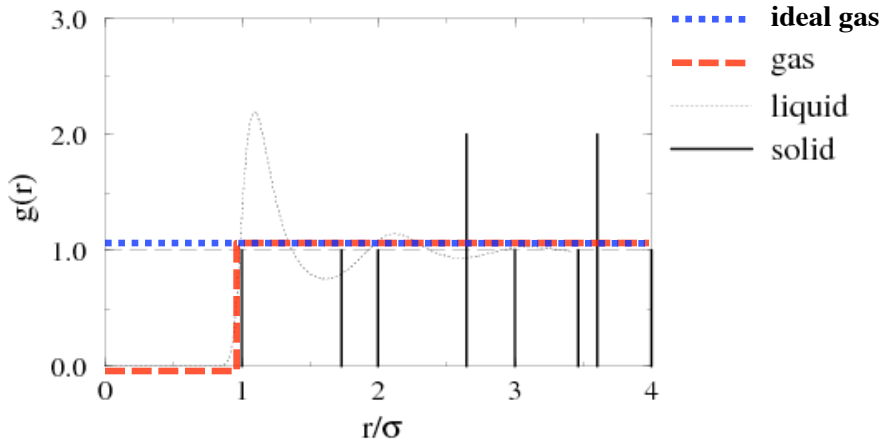
- The Radial distribution function, $g(r)$



solid



liquid



Liquid Structure, I

- Configurational distribution:

$$P(\mathbf{r}^N) = \frac{e^{-\beta U(\mathbf{r}^N)}}{\int d\mathbf{r}'^N e^{-\beta U(\mathbf{r}'^N)}}$$

- Specific joint probability distribution: [Particle 1 (2) at r_1 (r_2)]

$$\begin{aligned} P^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) &= \int d\mathbf{r}_3 \int d\mathbf{r}_4 \cdots \int d\mathbf{r}_N P(\mathbf{r}^N) \\ &= \int d\mathbf{r}'^N \delta(\mathbf{r}_1 - \mathbf{r}'_1)\, \delta(\mathbf{r}_2 - \mathbf{r}'_2)\, P(\mathbf{r}'^N) \\ &= \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1)\, \delta(\mathbf{r}_2 - \mathbf{r}'_2) \rangle \end{aligned}$$

- Generic reduced probability distribution function: (Any particle at r_1)

$$\rho^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \equiv N(N-1) P^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2)$$

- Generic *n*-point reduced probability distribution function (RPDF)

$$\rho^{(n/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) \equiv \frac{N!}{(N-n)!} \frac{\int d\mathbf{r}^{N-n} e^{-\beta U(\mathbf{r}^N)}}{\int d\mathbf{r}'^N e^{-\beta U(\mathbf{r}'^N)}}$$

Aside about Dirac vs. Kronecker Delta's

- Kronecker: (Discrete)

$$\delta_{ij} = \delta_{i,j} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases}$$

- Dirac: (Continuous)

$$\delta(x) = \lim_{a \to 0} \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx - |ak|} dx$$

$$\delta(x) = \lim_{a \to 0} \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}$$

Liquid Structure, II

- The 1-point RPDF is the density in an isotropic fluid:

$$\rho^{(1/N)}(\mathbf{r}_1) \overset{\text{iso}}{=} N\frac{\int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)}}{\int d\mathbf{r}'^N e^{-\beta U(\mathbf{r}'^N)}}$$

$$= N\frac{\int d\delta\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}_1,\delta\mathbf{r}^{N-1})}}{\int d\mathbf{r}_1 \int d\delta\mathbf{r}'^{N-1} e^{-\beta U(\mathbf{r}_1,\delta\mathbf{r}'^N)}}$$

$$= \frac{N}{\int d\mathbf{r}_1} = \frac{N}{V} = \rho$$

- The 2-point RPDF is also simple in an ideal gas
  - Separability reduces configurational distribution and the *n*-point specific reduced probability distribution:

$$P(\mathbf{r}^N) = \prod_{i=1}^{N} P(\mathbf{r}_i)$$

$$\rho^{(n/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{N!}{(N-n)!}\prod_{i=1}^{n} P(\mathbf{r}_i)$$

  - Hence the 2-point RPDF is:

$$\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) \overset{\text{id}}{=} \frac{N(N-1)}{V^2} \approx \rho^2$$

radial distribution function, $g(r)$

- Measure liquid structure according to how it deviates from the isotropic ideal gas limit:

$$g\left(\mathbf{r}_1,\mathbf{r}_2\right) \equiv \frac{\rho^{(2/N)}\left(\mathbf{r}_1,\mathbf{r}_2\right)}{\rho^2}$$

$$h\left(\mathbf{r}_1,\mathbf{r}_2\right) \equiv \frac{\rho^{(2/N)}\left(\mathbf{r}_1,\mathbf{r}_2\right)-\rho^2}{\rho^2}$$

- If the system is isotropic, then these quantities depend only on $\boldsymbol{r} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, and this leads to:

$$g(r) = g\left(\mathbf{r}_1,\mathbf{r}_2\right) \quad \text{the radial distribution function}$$
$$h(r) = g(r)-1 \quad \text{the pair correlation function}$$

- The challenge is: How does one calculate or measure *g(r)*?
  - Theory (e.g., integral equations, mode coupling theory, expansions)
  - Simulations
  - Experiment [FT of *g(r)* is related to the structure factor *S(q)*]

Potential of Mean Force

- Reversible Work Theorem: $\boxed{g(r) = e^{-\beta w(r)}}$
  - Where *w*(*r*) is the Helmholtz free energy (reversible work) to move a particle from infinity to a distance *r* from a chosen center
  - That is, the force on the particle in the fluid is: $F(r) = -\dfrac{\partial w}{\partial r}$
- Proof:

$$
\begin{aligned}
\langle F(r_{12})\rangle_{r_{12}} &= \left\langle -\tfrac{d}{dr_{12}} U(\vec{r}^{\,N}) \right\rangle_{r_{12}} , && \text{where } \vec{r}_{12} \equiv \vec{r}_2 - \vec{r}_1 \\
&= -\frac{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, \dfrac{\partial U}{\partial r_{12}} e^{-\beta U}}{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta U}} , && \text{for arbitrary } \vec{r}_1 \\
&= \frac{1}{\beta} \frac{\frac{\partial}{\partial r_{12}} \left\{ \int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta U} \right\}}{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta U}} \\
&= \frac{1}{\beta} \frac{\partial}{\partial r_{12}} \ln \left\{ \int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta U} \right\} \\
&= \frac{1}{\beta} \frac{\partial}{\partial r_{12}} \ln \left\{ \frac{N(N-1) \int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta U}}{\rho^2 \int d\vec{r}^{\,N} e^{-\beta U}} \right\} , && \text{by adding arb. constant} \\
&= \frac{1}{\beta} \frac{\partial}{\partial r_{12}} \ln \{ g(r_{12}) \} \\
&= -\frac{\partial}{\partial r_{12}} \ln \left\{ -\tfrac{1}{\beta} g(r_{12}) \right\} \\
\Longrightarrow \; w(r) &= -\tfrac{1}{\beta} \ln \{ g(r) \}
\end{aligned}
$$

- Take-Home Message:
  - A structural calculation of *g*(*r*) can lead to an understanding of forces

Integral Equations

- Ornstein-Zernike Equation:

$$h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13}) h(r_{23})$$

  - $h(r_{12})$: total (pair) correlation function [= $g(r)$-1]
  - $c(r_{12})$: direct correlation function

- Closures:

$$c(r) = g_{\text{total}}(r) - g_{\text{indirect}}(r)$$

  - Percus-Yevick:
  - Hypernetted Chain (HNC):
  - Many others!

$$c(r) \approx e^{-\beta w(r)} - e^{-\beta[w(r)-u(r)]}$$

$$c(r) \approx g(r) - w(r)$$

- Reference Interaction Site Model (RISM)
  - Anderson & Chandler, *JCP* **57**,1918 & 1930 (1972).
- RISM for ring polymers (PRISM)
  - Schweizer & Curro, *PRL* **58**, 246 (1987)

Computer simulations of $g(r)$

- Need force field, *e.g.,* Lennard-Jones

- Need a SamplingTechnique:
  - **Molecular Dynamics**
  - **Monte Carlo Sampling**

Computer simulations of $g(r)$

- **Molecular Dynamics**
  - Integration algorithm
    - Convergence w.r.t. step size
    - Convergence w.r.t. final time (ergodic?)
    - How do you assert convergence?
      - » Conservation of Energy?
      - » Reproducibility with time step?
      - » Conservation of symplectic norm
      - » Other?
  - Equilibrium & nonequilibrium averages
  - Constant T or S, P or V, μ or N Ensemble?
    - Stochastic forces?
    - Anderson barostats or Nose-Hoover thermostats
    - Langevin dissipation

Computer simulations of $g(r)$

- **Monte Carlo Sampling**
  - No real time averages!
  - Use Metropolis Monte Carlo
  - Choosing new configurations for the Metropolis step?
    - Pick initial arbitrary step size for particles
    - Optimize step size according to acceptance
    - Other types of moves???
    - REGARDLESS, need to ensure ergodic sampling!
  - Constant T ensembles
  - Constant μ or P ensembles?
    - "charging methods"
    - Widom insertion method