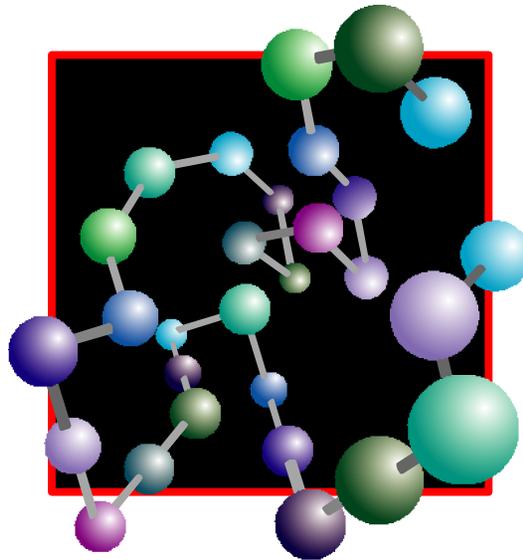


Introduction to polymer physics

Lecture 4

Boulder Summer School
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Ilya M. Lifshitz (1917-1982)

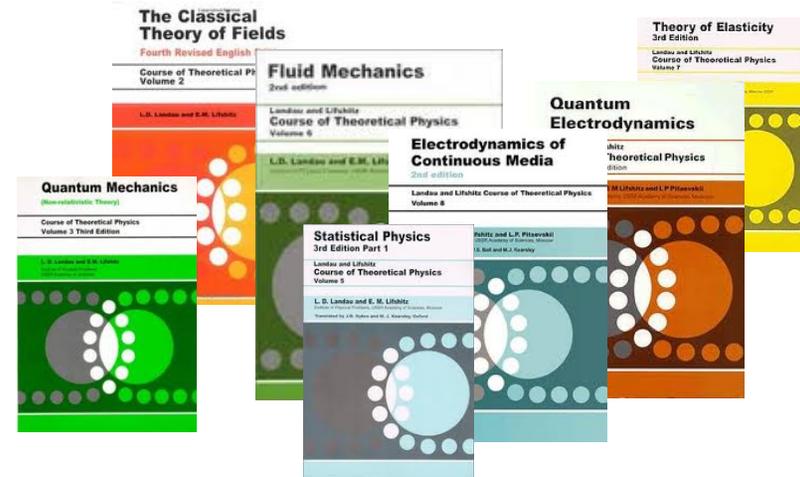
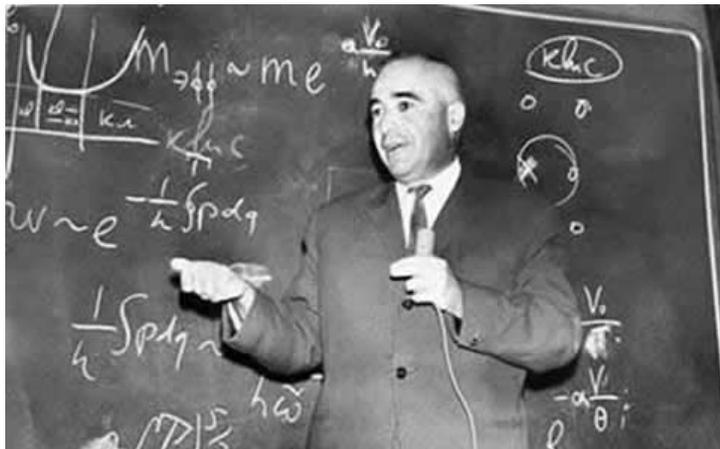


Fermi-surfaces, metals, disordered systems (optimal fluctuations, Lifshitz tails), supersolids, polymers...

Evgenii M. Lifshitz (1915-1985)



VdW interactions, Lifshitz point...



Lecture 4: A bit more mathematics

- Course outline:
- **Ideal chains** (Grosberg)
- **Real chains** (Rubinstein)
- **Solutions** (Rubinstein)
- **Methods** (Grosberg)
- **Closely connected:** interactions (Pincus), polyelectrolytes (Rubinstein), networks (Rabin), brushes (Zhulina), semiflexible polymers (MacKintosh)

- This lecture outline:
- Comment on Flory-Huggins
- Edwards Hamiltonian
- Polymers and classical mechanics (Semenov)
- Polymers and quantum mechanics (Lifshitz)
- Block-copolymers (Leibler)...

Comment on Flory-Huggins (1)

- Flory-Huggins interpretation:

$$\frac{\Delta F_{\text{mix}}}{nk_B T} = \overbrace{\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi)}^{\text{entropy of mixing}} + \overbrace{\chi\phi(1-\phi)}^{\text{energy of mixing}}$$

- Lifshitz (-like) interpretation:

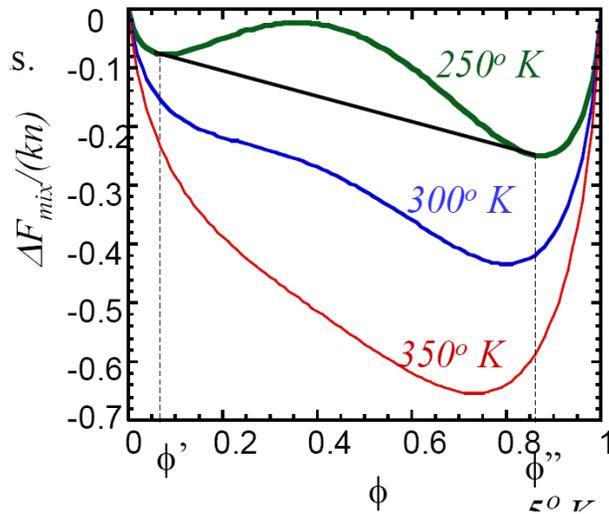
$$\frac{\Delta F_{\text{mix}}}{nk_B T} = \underbrace{\frac{\phi}{N_A} \ln \phi}_{\text{ideal gas of chains}} + \underbrace{\frac{1-\phi}{N_B} \ln(1-\phi) + \chi\phi(1-\phi)}_{\text{interaction part}}$$

- More phenomenological writing:

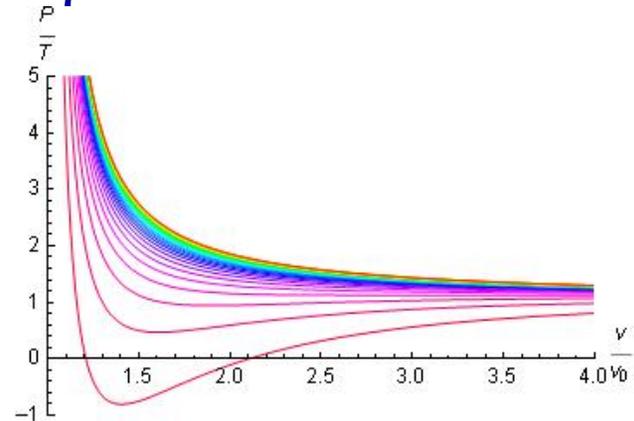
$$\frac{\Delta F_{\text{mix}}}{V k_B T} = \frac{c}{N_A} \ln(c v_0) + f_{\text{int}}(c)$$

Comment on Flory-Huggins (2)

- Van der Waals equation of state:

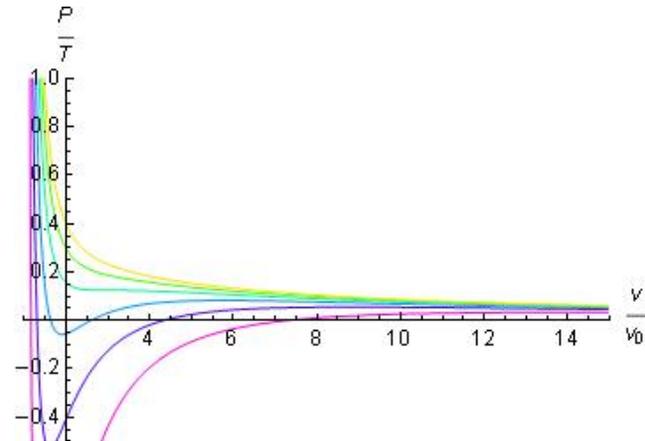
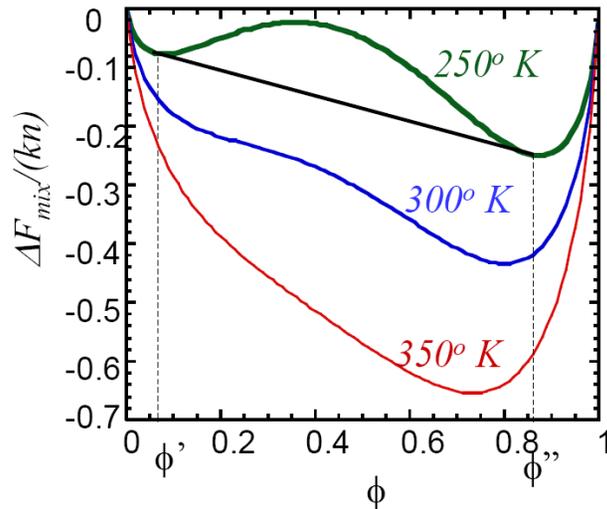


- Van der Waals equation of state:



Comment on Flory-Huggins (2)

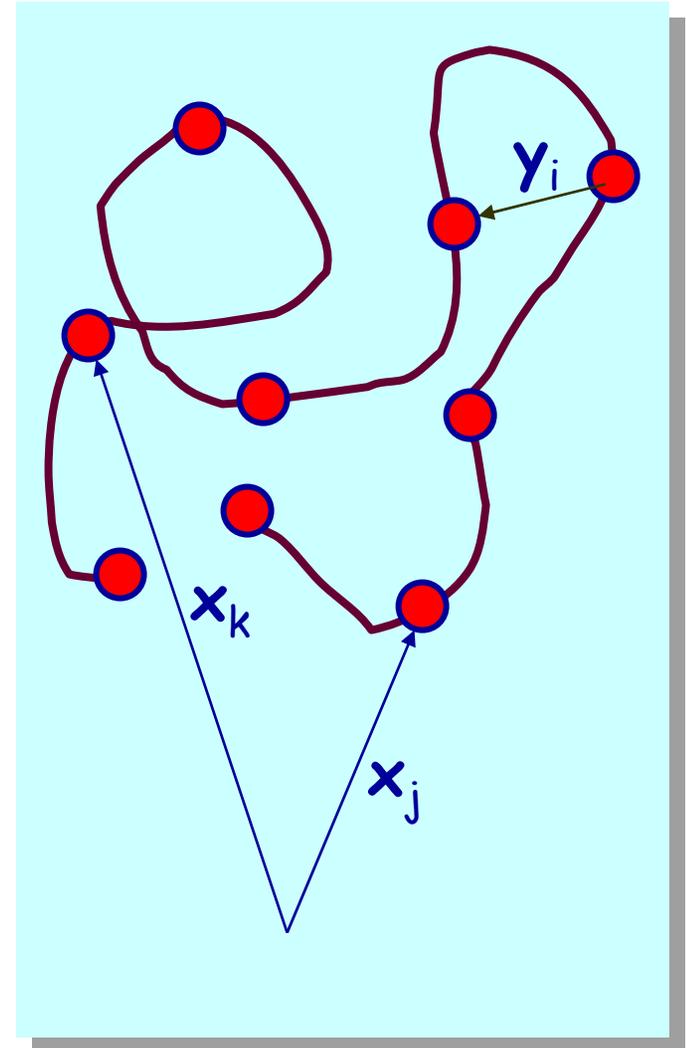
- FH free energy
- VdW equation of state



Exercises: (1) Re-interpret common tangent construction in terms of equation of state; (2) Develop a competing theory to Flory-Huggins based on VdW equation, discuss its advantages and disadvantages.

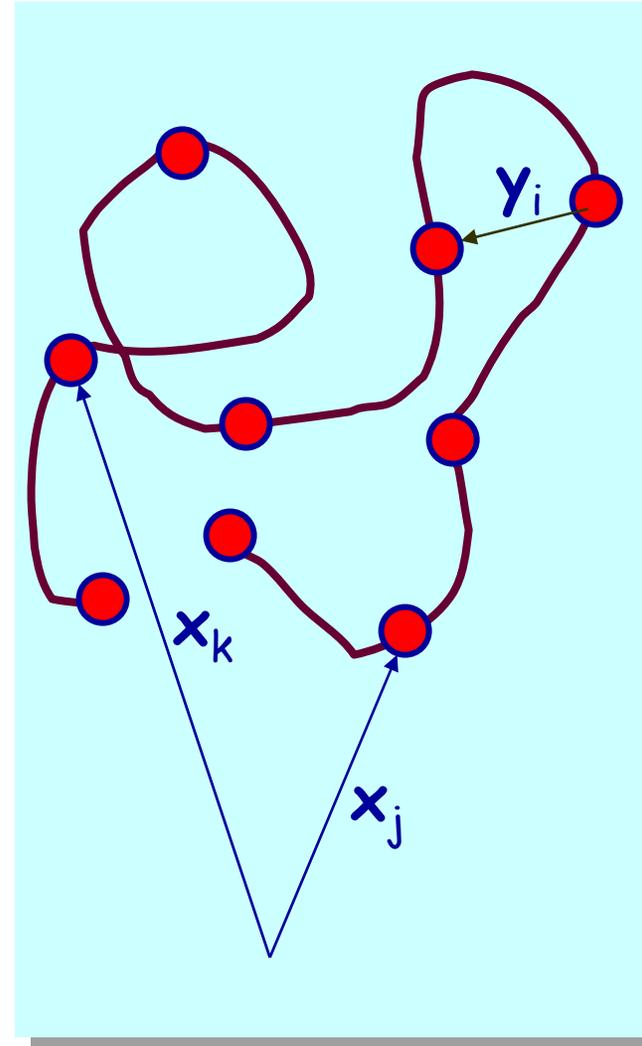
Ideal chain

- To begin with, suppose we are interested in only relatively few representative points:
- Position vectors of representative points are $\{\mathbf{x}_i\}$
- Suppose pieces between representative points are longer than Kuhn segment, then "bond vectors" $\{\mathbf{y}_i = \mathbf{x}_{i+1} - \mathbf{x}_i\}$ are (i) independent, and (ii) Gauss distributed:
$$g(\mathbf{y}) = (2\pi a^2/3)^{-3/2} \exp[-3\mathbf{y}^2/2a^2].$$
- Here a is not Kuhn segment, it depends on how many representatives we have.



Ideal chain (cont'd)

- Given independence and $g(\mathbf{y}) = (2\pi a^2/3)^{-3/2} \exp[-3\mathbf{y}^2/2a^2]$, probability distribution of the whole conformation on this level of description reads $G(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = g(\mathbf{y}_1)g(\mathbf{y}_2) \dots g(\mathbf{y}_{n-1})$. This multiplicative structure is the signature of ideal chain.



Generalization

- In general, $\{x_i\}$ may include more than just coordinates of representative points, e.g., orientation/direction, internal state (helix-coil), etc.

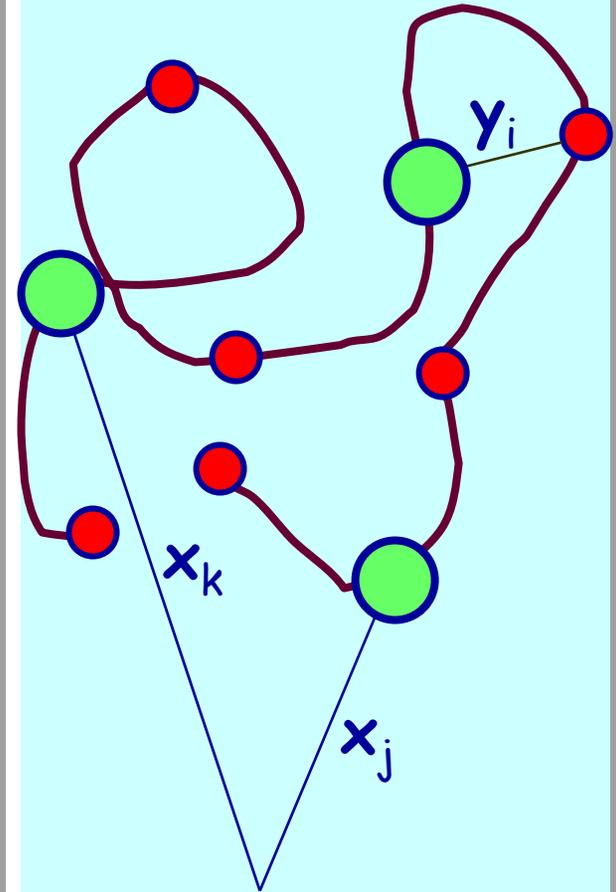
$$G(x_1, x_2, \dots, x_n) = g(x_1, x_2)g(x_2, x_3) \dots g(x_{n-1}, x_n).$$

This multiplicative structure is still the signature of ideal chain.

- Here $g(x, x')$ is conditional probability, it satisfies $\int g(x, x') dx' = 1$
- Note of care: bonds are NOT in equilibrium

Comments:

- Although $g(\mathbf{y}) \sim \exp[-3\mathbf{y}^2/2a^2]$ is exponential, it is not right to interpret $g(\mathbf{y})$ as equilibrium Boltzmann probability $\exp(-\text{energy}/k_B T)$, because it is not energy, it is entropic spring. As a result, there is no temperature.
- If G and g are viewed as TD probabilities, then normalization condition means that free unrestricted ideal chain is taken as zero level of free energy.
- Imagine we want to switch to a less detailed description, with fewer representative points $\{X_i\}$; then



$$\tilde{g}(X, X') = \int g(X, x_1)g(x_1, x_2) \dots g(x_k, X')dx_1dx_2 \dots dx_k$$

Equation

- Green's function

$$G \left(\begin{array}{c|c} 1 & n \\ x & x' \end{array} \right)$$

- We can find it by integrating over all intermediate $\{x_i\}$.
- It satisfies equation

$$G \left(\begin{array}{c|c} 1 & n+1 \\ x & x'' \end{array} \right) = \int G \left(\begin{array}{c|c} 1 & n \\ x & x' \end{array} \right) g(x', x'') dx'$$

$$G_{n+1} = \hat{g} G_n$$

Operator

$$G_{n+1} = \hat{g}G_n$$

- If x is just coordinates and

$$g(y) \sim \exp[-3y^2/2a^2]$$

- Then $\hat{g} = \exp\left[\frac{a^2}{6}\Delta\right] \implies G_{n+1} = \exp\left[\frac{a^2}{6}\Delta\right] G_n$

- (think of k -representation, $\exp[-k^2a^2/6]$)

- Under proper conditions $G_{n+1} \approx G_n + \partial_n G_n$ and $\exp((a^2/6)\Delta) \approx 1 + (a^2/6)\Delta$ then

$$\partial_n G_n = (a^2/6)\Delta G_n$$

Diffusion equation

$$G_{n+1} = \hat{g}G_n$$

$$\hat{g} = \exp\left[\frac{a^2}{6}\Delta\right] \implies G_{n+1} = \exp\left[\frac{a^2}{6}\Delta\right] G_n$$

- Under proper conditions $G_{n+1} \approx G_n + \partial_n G_n$ and $\exp((a^2/6)\Delta) \approx 1 + (a^2/6)\Delta$ then $\partial_n G_n = (a^2/6)\Delta G_n$
- Diffusion equation returns the well known solution

$$G_n(\mathbf{x}, \mathbf{x}') \sim \exp[-(3/2na^2)(\mathbf{x} - \mathbf{x}')^2]$$

no new information: what we put in - we got out

Challenging exercise: Find operator g for worm-like chain.
Hint: in this case, $\mathbf{x} = \{\mathbf{x}, n\}$

Continuum limit

- Given

$$g(\mathbf{y}) \sim \exp[-3\mathbf{y}^2/2a^2],$$

probability of conformation

$$G(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = g(\mathbf{y}_1)g(\mathbf{y}_2) \dots g(\mathbf{y}_{n-1})$$

$$\sim \exp[-3[(\mathbf{x}_1 - \mathbf{x}_2)^2 + (\mathbf{x}_2 - \mathbf{x}_3)^2 + \dots + (\mathbf{x}_{n-1} - \mathbf{x}_n)^2]/2a^2]$$

$$= \exp(-\int [3(\partial\mathbf{x}/\partial s)^2/2a^2] ds)$$

- Looks very much like

$$\exp[(i/\hbar)\int [\text{kinetic energy}] dt]$$

Green's function in continuum limit

- When we integrate over all intermediate $\{x_i\}$ in

$$G(x_1, x_2, \dots, x_n) \sim \exp[-3[(x_1 - x_2)^2 + (x_2 - x_3)^2 + \dots + (x_{n-1} - x_n)^2]/2a^2]$$
$$= \exp(-\int [3(\partial x / \partial s)^2 / 2a^2] ds)$$

we arrive at path integral:

$$G_n(x, x') = \int \exp(-\int [3(\partial x / \partial s)^2 / 2a^2] ds) D\mathbf{x}(s)$$

- This is the partition sum of our polymer - the sum over all conformations.
- In this continuum form, it satisfies $\partial_n G_n = (a^2/6)\Delta G_n$
- Thus, we can do cont. limit via $G_{n+1} \approx G_n + \partial_n G_n$ and $\exp((a^2/6)\Delta) \approx 1 + (a^2/6)\Delta$ or via path integral

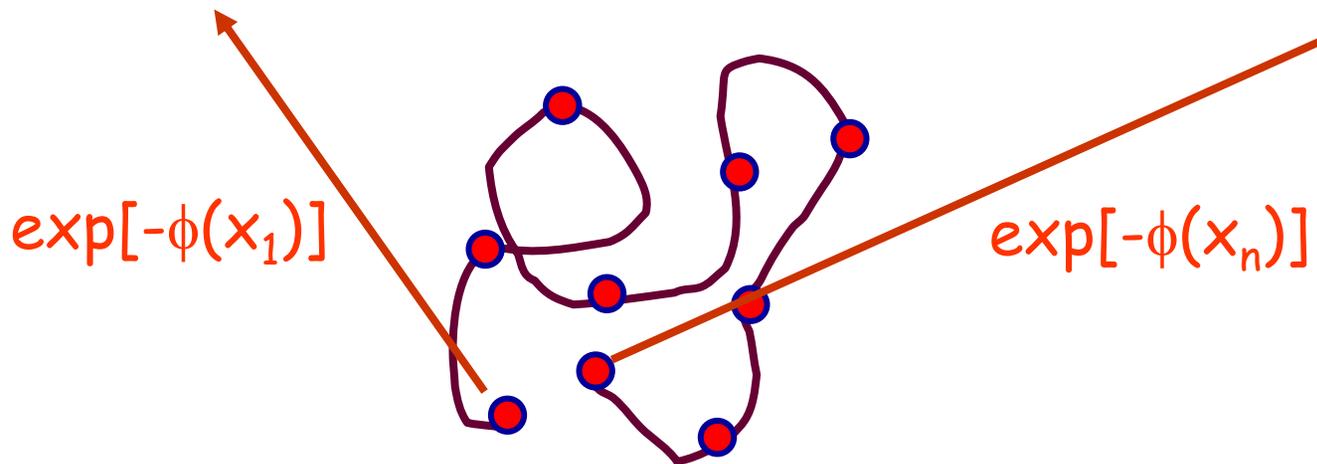
A bit more general: $\phi(x)$

- Still assume ideal polymer, but suppose each monomer (really -- representative point) carries energy $\phi(x)$ which depends on position (or in general on x).
Instead of

$$G(x_1, x_2, \dots, x_n) = g(x_1, x_2)g(x_2, x_3) \dots g(x_{n-1}, x_n).$$

we now have (assuming $k_B T = 1$)

$$G(x_1, x_2, \dots, x_n) = g(x_1, x_2)e^{-\phi(x_2)}g(x_2, x_3)e^{-\phi(x_3)} \dots e^{-\phi(x_{n-1})}g(x_{n-1}, x_n).$$



Continuum limit with $\phi(x)$

- We had

$$G(x_1, x_2, \dots, x_n) \sim \exp[-3[(x_1 - x_2)^2 + (x_2 - x_3)^2 + \dots + (x_{n-1} - x_n)^2]/2a^2]$$
$$= \exp(-\int [3(\partial x / \partial s)^2 / 2a^2] ds)$$

- Now we insert $\phi(x)$ in the exponential:

Continuum limit with $\phi(x)$

- We had
$$G(x_1, x_2, \dots, x_n) \sim \exp[-3[(x_1 - x_2)^2 + (x_2 - x_3)^2 + \dots + (x_{n-1} - x_n)^2]/2a^2]$$
$$= \exp(-\int [3(\partial x / \partial s)^2 / 2a^2] ds)$$
- Now we insert $\phi(x)$ in every point in the exponential:

Continuum limit with $\phi(x)$

- We had
$$G(x_1, x_2, \dots, x_n) \sim \exp[-3[(x_1 - x_2)^2 + (x_2 - x_3)^2 + \dots + (x_{n-1} - x_n)^2]/2a^2]$$
$$= \exp(-\int [3(\partial x / \partial s)^2 / 2a^2] ds)$$

$\phi(x_1)$ $\phi(x_2)$ $\phi(x_3)$ $\phi(x_n)$
↓ ↓ ↓ ↓
- Now we insert $\phi(x)$ in every point in the exponential and arrive at
$$G(x_1, x_2, \dots, x_n) \sim \exp(-\int [3(\partial x / \partial s)^2 / 2a^2 + \phi(x(s))] ds)$$

↑
- Looks very much like
$$\exp[(i/\hbar) \int [\text{kinetic energy} - \text{potential energy}] dt]$$

except for disturbing sign difference!

Green's function with $\phi(x)$

- Green's function is the sum over all conformations with fixed ends - path integral:

$$G_n(\mathbf{x}, \mathbf{x}') = \int \exp(-\int [3(\partial\mathbf{x}/\partial s)^2/2a^2 + \phi(\mathbf{x}(s))] ds) D\mathbf{x}(s)$$

- This is partition sum of the chain with fixed ends

- Looks very much like, but simpler than $\int \exp[(i/\hbar)\int [\text{kinetic energy} - \text{potential energy}] dt] D\mathbf{x}(t)$ except for disturbing sign difference!

Applicability of cont. limit

- Nothing changes significantly over the length scale of Kuhn segment.
- Let $\phi(x)$ change over length scale $\lambda \gg b$. Then we can choose equivalent chain with $\lambda \gg a \gg b$

- Because $a \gg b$, we can approximate $g(y)$ as Gaussian
- Because $\lambda \gg a$, we have $a^2 \Delta \sim a^2 / \lambda^2 \ll 1$, and we can expand
$$\exp((a^2/6)\Delta) \approx 1 + (a^2/6)\Delta$$

Edwards Hamiltonian

- Green's function is the sum over all conformations with fixed ends - path integral:

$$G_n(\mathbf{x}, \mathbf{x}') = \int \exp(-\int [3(\partial\mathbf{x}/\partial s)^2/2a^2 + \phi(\mathbf{x}(s))] ds) D\mathbf{x}(s)$$

- External or self-consistent field

$$\mathcal{H}_0 = \frac{3}{2a^2} \int_0^L \dot{\mathbf{x}}^2(s) ds + \int_0^L \phi(\mathbf{x}(s)) ds$$

- Two body interaction

$$\mathcal{H} = \frac{3}{2a^2} \int_0^L \dot{\mathbf{x}}^2(s) ds + \frac{1}{2} \int_0^L \int_0^L V(\mathbf{x}(s) - \mathbf{x}(s')) ds ds'$$

- Very short ranged potential

$$\mathcal{H} = \frac{3}{2a^2} \int_0^L \dot{\mathbf{x}}^2(s) ds + \frac{v}{2} \int_0^L \int_0^L \delta(\mathbf{x}(s) - \mathbf{x}(s')) ds ds'$$

Example 1

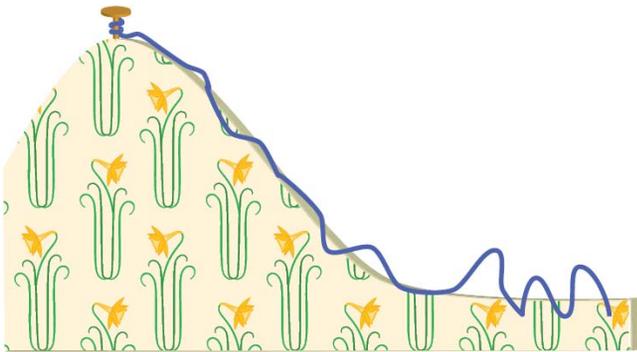
- Imagine a polymer pinned down by one end at the top of a potential bump (e.g., Flagstaff mountain), and hanging down from there.
- If the potential is strong and temperature low, the most probable conformation will correspond to the minimum of the expression in the exponent

$$G(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \sim \exp(-\int [3(\partial\mathbf{x}/\partial s)^2/2a^2 + \phi(\mathbf{x}(s))] ds)$$

- i.e. $\mathbf{x}(s)$ corresponds to

$$\min \int [3(\partial\mathbf{x}/\partial s)^2/2a^2 + \phi(\mathbf{x}(s))] ds$$

A.N. Semenov, Sov. Phys. JETP, 61, p. 733, 1985



Example 1 (cont'd)

- i.e. $x(s)$ corresponds to

$$\min \int [3(\partial \mathbf{x} / \partial s)^2 / 2a^2 + \phi(\mathbf{x}(s))] ds$$

- This looks exactly like: if classical mechanics applies, then particle chooses trajectory $x(t)$ such as to minimize action

$$\min \int [m(\partial \mathbf{x} / \partial t)^2 / 2 - U(\mathbf{x}(t))] dt$$

- Dictionary: $s \rightarrow t$, $3/a^2 \rightarrow m$, $\partial \mathbf{x} / \partial s \rightarrow v$, $\phi(\mathbf{x}) \rightarrow -U(\mathbf{x})$.
It is surprising, but has physical meaning that $\phi(\mathbf{x})$ is MINUS potential.

Example 1 (cont'd further)

- Optimal trajectory in mechanics satisfies $F=ma$ or $mv^2/2+U=const$
- Optimal conformation of a polymer satisfies

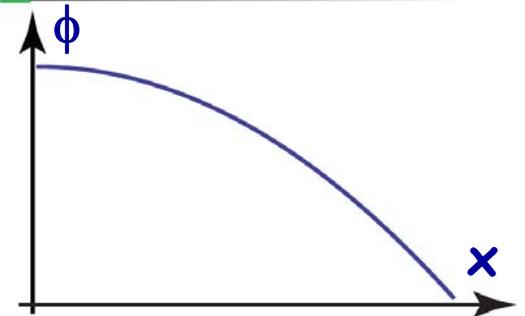
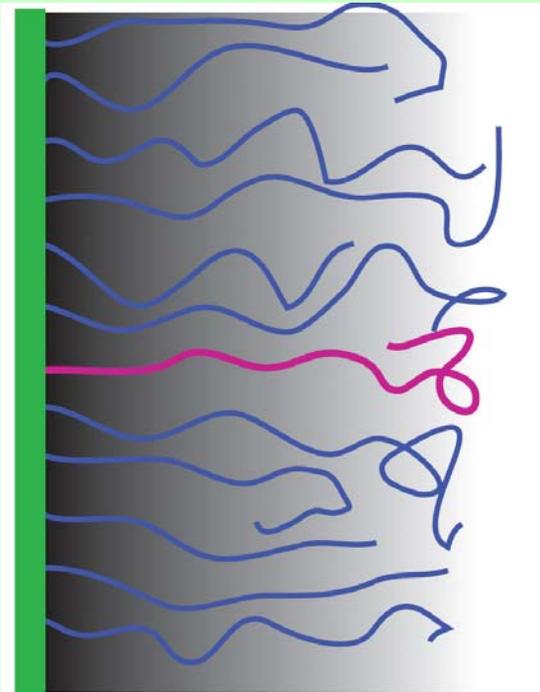
$$\nabla \frac{\phi}{k_B T} = \frac{3}{a^2} \ddot{x} \Leftrightarrow \frac{3k_B T}{2a^2} \dot{x}^2 - \phi(x) = E$$

- Per little chain piece δs : $\frac{3k_B T}{2a^2} \frac{\delta x^2}{\delta s} - \phi(x)\delta s = E\delta s$
i.e., chain stretching energy is large at large potential and small where potential is small, thus $\phi(x)$ is analogous to $-U(x)$.
- Free energy $F=-k_B T \ln G$ reads

$$F = \int_0^N \left[\frac{3k_B T}{2a^2} \dot{x}^2(s) + \phi(x(s)) \right] ds$$

First serious application

- Consider a brush, and look at one chain there. It cannot wiggle sideways because of peer pressure. There is some sort of a (self-consistent) field $\phi(x)$, where x is height above the plane, which favors chain rushing up, to better life. What is this field?
- Every chain is a "particle" that starts at $x=0$ and reaches some height $x=h$, different for different chains, in one and the same "time" $t=N...$

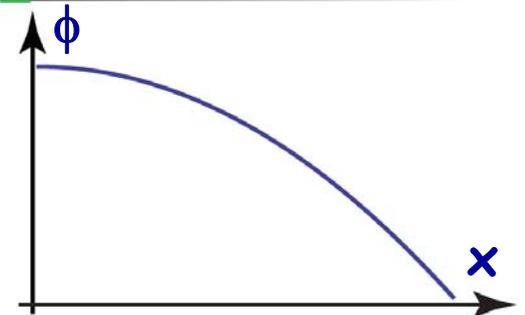
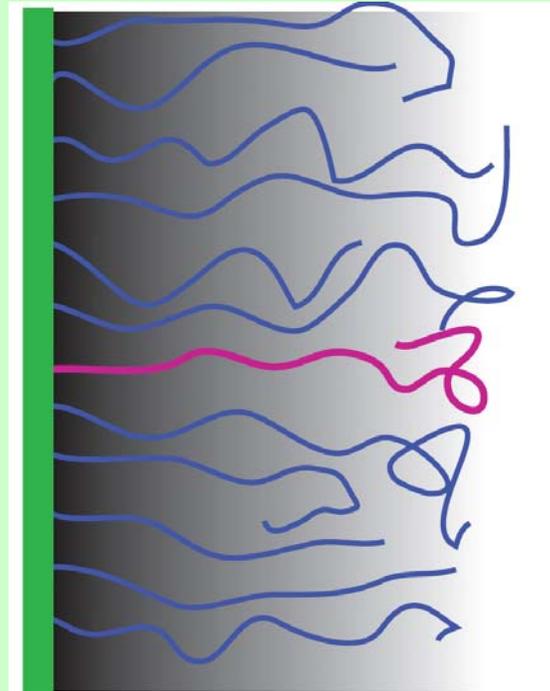


Isochronous pendulum

- Reverse: the time (period) does not depend on height (amplitude). Isochronous pendulum!!!
- For a harmonic oscillator, $\omega = (k/m)^{1/2}$ independently of amplitude; this is true for harmonic oscillator ONLY.
- For real pendulum, period becomes longer at very large amplitudes.



As
candelabra
swings
more, does
it also
swing
faster?



Potential in the brush

Thus, brush is like a harmonic oscillator, $U(x) \sim x^2$ or
 $\phi(x) \sim -x^2$

Famous "parabolic profile"

It is very clever that $\phi(x) \rightarrow -U(x)$, because $\phi(x)$ in the brush must be a bump

We can even establish coefficient in $\phi(x) = -kx^2/2$, because quarter-period is N : $k = (3\pi^2/4)(k_B T/N^2 a^2)$

In this form, the argument is due to S.T.Milner, T.A.Witten, and M.E.Cates *Europhys. Lett.*, **5** (5), pp. 413-418 (1988) "A Parabolic Density Profile for Grafted Polymers".

E.Zhulina in her lecture is likely to present another independently developed view on the same topic

Potential and density

Given the harmonic oscillator potential

$$\phi(x) = -\frac{3\pi^2}{8} \frac{k_B T}{N^2 a^2} x^2$$

the "particle energy conservation" reads

$$\frac{3k_B T}{2a^2} \dot{x}^2 - \phi(x) = E \Leftrightarrow \frac{3k_B T}{2a^2} \dot{x}^2 = E - \frac{kx^2}{2}$$

"Total energy" is established from boundary condition that "particle" arrives to the amplitude position at zero velocity, or chain is not stretched at the end:

$$\dot{x} = \frac{\pi}{2N} \sqrt{h^2 - x^2}$$

Density: #monomers δs per height interval δx : $\delta s / \delta x$, i.e., inverted velocity:

$$\rho_1(x, h) = \frac{2N}{\pi} \frac{1}{\sqrt{h^2 - x^2}}$$

Density

Inverted velocity is density of one chain whose end is located at given height h :

$$\rho_1(x, h) = \frac{2N}{\pi} \frac{1}{\sqrt{h^2 - x^2}}$$

Different chains end at different heights h . Given σ chains per unit area, total density is the sum:

$$\rho(x) = \sigma \int_0^H \rho_1(x, h) \psi(h) dh ,$$

where H is total brush height (maximal h), and $\psi(h)$ is the fraction of chains ending at h - both to be found from the self-consistency condition which relates field $\phi(x)$ to the total density $\rho(x)$: $\phi(x) - \phi(H) = k_B T v \rho(x)$

Exercise: Show that for a chain with free end at the height h , monomer number s is located on average at the height $x = h \sin(\pi s / 2N)$

Self-consistency

Self-consistency condition relates field $\phi(x)$ to the total density $\rho(x)$: $\phi(x) - \phi(H) = k_B T v \rho(x)$:

$$\phi(x) - \phi(H) = k_B T v \sigma \int_0^H \rho_1(x, h) \psi(h) dh .$$

Since we know both $\phi(x)$ and $\rho_1(x, h)$, we get equation:

$$\frac{3\pi^2}{8N^2 a^2} (H^2 - x^2) = \frac{2v\sigma N}{\pi} \int_0^H \frac{\psi(h) dh}{\sqrt{h^2 - x^2}} .$$

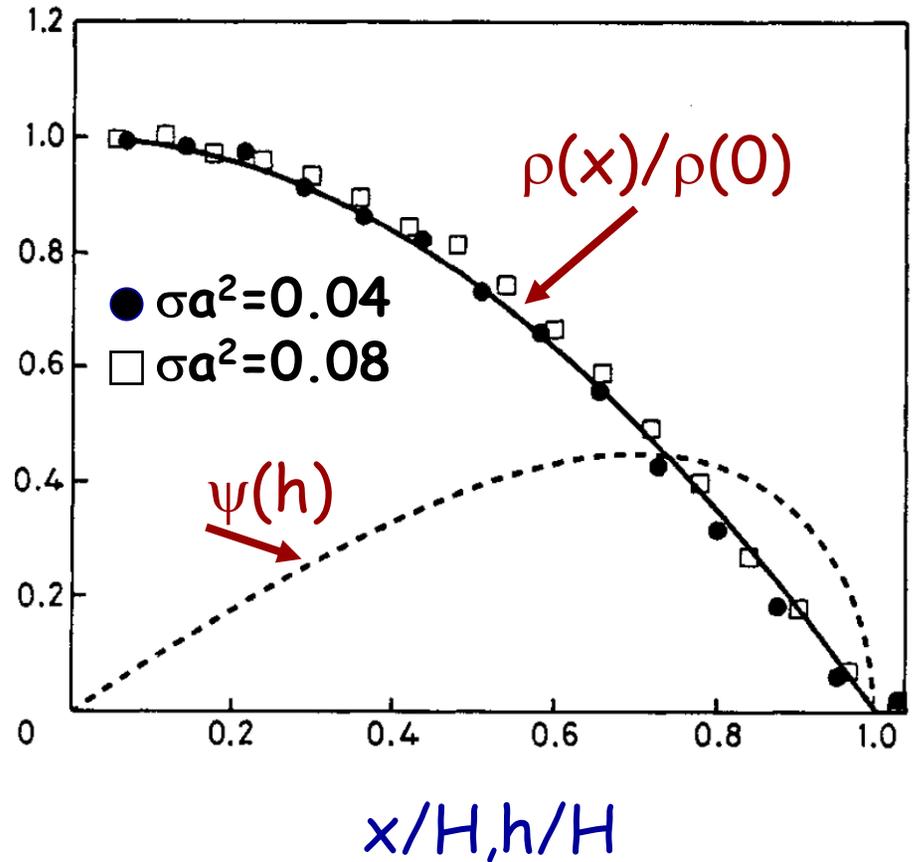
The rest is a few lines of algebra. Integrate both sides over h from 0 to H to get

$$H = N \left(\frac{4a^2 v \sigma}{\pi^2} \right)^{1/3} \quad \text{and then} \quad \psi(h) = \frac{3}{H^3} h \sqrt{H^2 - h^2}$$

This completes the mean field solution.

Results for brush:

- Figure from Milner-Witten-Cates, EPL 1988



Applicability of mean field

- Mean field applies if thermal blob g_T (the distance needed to develop self-avoidance correlations) is larger than the distance g' to the neighboring chains.
- The former is estimated from $vg^{1/2}/a^3 \sim 1$, the latter from $a^2g \sim 1/\sigma$
- Thus the conditions: $v^2/a^6 \ll \sigma a^2 \ll 1$

Green's function with $\phi(\mathbf{x})$

(repeated)

- Green's function is the sum over all conformations with fixed ends - path integral:
$$G_n(\mathbf{x}, \mathbf{x}') = \int \exp(-\int [3(\partial\mathbf{x}/\partial s)^2/2a^2 + \phi(\mathbf{x}(s))] ds) D\mathbf{x}(s)$$
- This is partition sum of the chain with fixed ends
- Looks very much like, but simpler than
$$\int \exp[(i/\hbar)\int [\text{kinetic energy} - \text{potential energy}] dt] D\mathbf{x}(t)$$

except for disturbing sign difference!
- In QM, it satisfies Schroedinger equation. By analogy,

$$\frac{\partial G_n}{\partial n} = \frac{a^2}{6} \Delta G_n - \phi(\mathbf{x}) G_n$$

Bilinear expansion

$$\frac{\partial G_n}{\partial n} = \frac{a^2}{6} \Delta G_n - \phi(\mathbf{x}) G_n$$

- Since it looks like Schroedinger equation, let us proceed as we are taught in QM: expand x-dependence over eigenmodes $-\lambda_k \psi_k(x) = \frac{a^2}{6} \Delta \psi_k - \phi(x) \psi_k$

$$G_n(x, x') = \sum_k C_k(n) \psi_k(x) \psi_k(x')$$

- Then

$$\frac{\partial C_k(n)}{\partial n} = -\lambda_k C_k(n) \implies C_k(n) = e^{-n\lambda_k}$$

Ground state dominance

- If there is discrete "energy level", then largest | (smallest energy) dominates and

$$G_n(x, x') \simeq e^{-\lambda n} \psi(x) \psi(x')$$

- where λ and ψ are "ground state energy" and "wave function" of

$$\frac{\hbar^2}{2m} \Delta \psi + (\lambda - \phi(x)) \psi = 0$$

- Reminder from QM: wave function of ground state can be always chosen positive (has no zeros).
- Examples: chain in a box, in a tube, in a slit, etc

Phase transition

- Remember that $\phi(x) \rightarrow \phi(x)/k_B T$. Presence or absence of discrete level is determined by temperature:

$$\frac{a^2}{6} \Delta \psi + \left(\lambda - \frac{\phi(x)}{k_B T} \right) \psi = 0$$

- Challenging exercises: (1) Suppose field $f(x)$ is some potential well in 3D, but $\phi(x)=0$ outside a certain finite volume (or rapidly goes to zero). What is the order of phase transition? (2) Suppose field $\phi(x)$ depends only on one coordinate, say z , and is equal to zero outside finite interval of z ; is there phase transition? (3) Suppose field $\phi(x)$ depends only on one coordinate, say z , and is equal to infinity at $z<0$, zero at $z>A$, and some negative value between $z=0$ and $z=A$; is there phase transition?

Free energy, density

- Given that $G_n(x, x') \simeq e^{-\lambda n} \psi(x) \psi(x')$ free energy is $F = TN\lambda$

- To find density, consider

$$G \left(\begin{array}{c|c|c} 1 & M & N \\ \hline x' & x & x'' \end{array} \right) \simeq e^{\lambda M} \psi(x') \psi(x) e^{\lambda(N-M)} \psi(x) \psi(x'')$$

- Thus, $n(x) = \psi^2(x)$ (assuming ψ is properly normalized)

$$\frac{a^2}{6} \Delta \psi + \left(\lambda - \frac{\phi(x)}{T} \right) \psi = 0$$

Entropy

- We know free energy is $F=TN\lambda$ and density $n(x)=\psi^2(x)$
- Entropy:

$$\begin{aligned} S = \frac{E - F}{k_B T} &= (n, \frac{\phi}{T}) - (n, \lambda) = (\psi^2, \frac{\phi}{T} - \lambda) = (\psi, \underbrace{(\frac{\phi}{T} - \lambda)\psi}_{(a^2/6)\Delta\psi}) \\ &= \frac{a^2}{6}(\psi, \Delta\psi) \end{aligned}$$

- Notes: (1) ψ is an order parameter; (2) $S \sim Na^2/R^2$ is recovered.

$$\frac{a^2}{6} \Delta\psi + (\lambda - \frac{\phi(x)}{T})\psi = 0$$

Self-consistency

- Particle which digs well for itself.
- Free energy:

$$F = \int f^*(\psi^2) d^3x - T \frac{a^2}{6} \int \psi \Delta \psi d^3x$$

- Minimize this with respect to ψ , with Lagrange multiplier λ ensuring that ψ is properly normalized:

$$\frac{a^2}{6} \Delta \psi + \left(\lambda - \frac{\mu^*}{T} \right) \psi = 0$$

- Equilibrium free energy:

$$F = \lambda NT + (f^* - n\mu^*, 1) = \lambda NT - (p^*, 1)$$

Virial expansion

$$\frac{a^2}{6} \Delta \psi + \left(\lambda - \frac{\mu^*}{T} \right) \psi = 0$$

- Virial expansion for μ^*

$$\frac{a^2}{6} \Delta \psi + (\lambda - B\psi^2 - C\psi^4) \psi = 0$$

Solution for large globule

$$\frac{a^2}{6} \Delta \psi + (\lambda - B\psi^2 - C\psi^4)\psi = 0$$

- In the interior, $\psi = \text{const}$: $\lambda = B\psi^2 + C\psi^4 = Bn + Cn^2$
- Equilibrium free energy: $(1/2)Bn^2 + (1/3)Cn^3$, has minimum at $B < 0$ at $n \sim -B/C$: exactly the same answer as before.
- In the surface layer, full non-linear PDE has to be addressed.

Challenging problem

- Consider polymer with excluded volume, but no attractions ($B>0, C>0$) collapsed in a potential box with infinite walls. What is the profile of the self-consistent potential μ^* ?

$$\frac{a^2}{6} \Delta \psi + \left(\lambda - \frac{\mu^*}{T} \right) \psi = 0$$

Summary

- Chain connectivity is one thing and interactions is the other: this is a possible and fruitful point of view.
- “Quasi-classical” limit for stretched chains.
- “Ultra-quantum” limit for collapse.
- One has to watch for physics not only doing magic estimates, but also performing routine calculations.