Physics 850: Soft Condensed Matter Physics, Fall04
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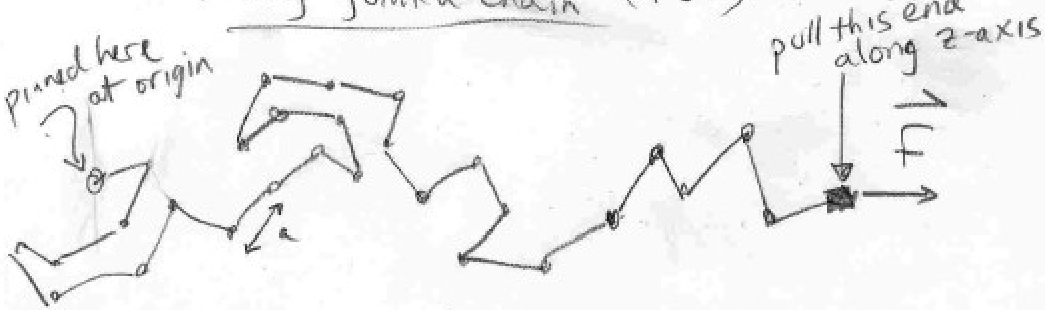
Lecture 6: Freely Jointed Chain

A more precise look at the ideal chain model:

Freely jointed chain (FJC)



- Each segment is stiff, but connected by free hinge to neighbors.
- One end is held to a point, other end fluctuates if it is let go.
  → If one holds the other end, how much force (F) needs to be applied? (restoring force of polymer, $-\vec{F}$, may be viewed as entropic force)

- let $\hat{t}_i$ = tangent vector along i^{th} chain.
- Energy = work done on chain to hold its length
  $$E = -\vec{f}\cdot\vec{r}_N \quad , \vec{r}_N = \text{vector from end to end}$$
- $\vec{r}_N = a\sum_i \hat{t}_i$ (N = # segments)
  so $E = -fa\left(\sum_i \hat{t}_i\cdot\hat{z}\right)$

  direction of force

... FJC ...

Probability of each configuration $\{\hat{t}_i\}$

$$P = \frac{e^{-E/KT}}{Q} = \frac{1}{Q} e^{\frac{fa}{KT}\sum_i \hat{t}_i \cdot \hat{z}}$$

Average end-to-end length along $\vec{f}$ direction:

$$\langle z \rangle = \underbrace{\sum_{\hat{t}_i}}_{\text{sum on all configurations}} \underbrace{\frac{1}{Q} e^{\frac{fa}{KT}\left(\sum_j \hat{t}_j \cdot \hat{z}\right)}}_{P(z)} \cdot \underbrace{a\left(\sum_j \hat{t}_j \cdot \hat{z}\right)}_{z}$$

$$= \frac{1}{KT}\frac{1}{Q}\frac{\partial}{\partial f}\sum_{\hat{t}_i} e^{\frac{fa}{KT}\left(\sum \hat{t}_i \cdot \hat{z}\right)}$$

use $Q = \sum_x e^{-E_x/KT}$ & $\frac{1}{Q}\frac{\partial Q}{\partial f} = \frac{\partial \ln Q}{\partial f}$

$$= \frac{1}{KT}\frac{\partial}{\partial f}\ln \sum_{\hat{t}_i} e^{\frac{fa}{KT}\left(\sum \hat{t}_i \cdot \hat{z}\right)}$$

$$= \frac{1}{KT}\frac{\partial}{\partial f}\ln\left\{\sum_{\hat{t}_1} e^{\frac{fa}{KT}\hat{t}_1 \cdot \hat{z}} \cdot \sum_{\hat{t}_2} e^{\frac{fa}{KT}\hat{t}_2 \cdot \hat{z}} \cdot \sum_{\hat{t}_3} \cdots\right)$$

Since chains are uncorrelated, each factor is the same.

$$\rightarrow \langle z \rangle = \frac{1}{KT}\frac{\partial}{\partial f}\ln\left\{\underbrace{\int_{-1}^{1} d(\cos\theta)\int_0^{2\pi} d\phi}_{=\int_0^{\pi}\sin\theta d\theta \int_0^{2\pi} d\phi} e^{\frac{fa}{KT}\cos\theta}\right\}^N$$

$$= \frac{1}{KT}\frac{\partial}{\partial f}\ln\left\{2\pi \cdot \frac{KT}{fa}\left(e^{\frac{fa}{KT}} - e^{-\frac{fa}{KT}}\right)\right\}^N$$

↓

... FJC ...

$$\langle z\rangle = \frac{1}{kT}\frac{\partial}{\partial f}\left\{-N\ln\frac{fa}{kT} + N\ln\left(e^{\frac{fa}{kT}} - e^{-\frac{fa}{kT}}\right)\right\}$$

$$= \frac{1}{kT}\left\{-N\left(\frac{1}{f}\right) + N\,\frac{\frac{a}{kT}\left(e^{\frac{fa}{kT}} + e^{-\frac{fa}{kT}}\right)}{e^{\frac{fa}{kT}} - e^{-\frac{fa}{kT}}}\right\}$$

$$\langle z\rangle = aN\left(-\frac{1}{fa/kT} + \coth\frac{fa}{kT}\right)$$

(see plot)

Small forces:

let $\frac{fa}{k_BT} = \eta$ (dimensionless)

$$\langle z\rangle = aN\left[-\frac{1}{\eta} + \frac{e^{\eta}+e^{-\eta}}{e^{\eta}-e^{-\eta}}\right]$$

$$z \ll 1 \rightarrow \langle z\rangle = aN\left[\frac{-1}{\eta} + \frac{1+\eta+\frac{\eta^2}{2}+\frac{\eta^3}{6} + 1-\eta+\frac{\eta^2}{2}-\frac{\eta^3}{6}+\dots}{\cancel{1}+\eta+\cancel{\frac{\eta^2}{2}}+\frac{\eta^3}{6} - \left(\cancel{1}-\eta+\cancel{\frac{\eta^2}{2}}-\frac{\eta^3}{6}+\dots\right)}\right]$$

$$\langle z\rangle \simeq aN\left[\frac{-1}{\eta} + \frac{\cancel{2}\left(1+\frac{\eta^2}{2}\right)}{\cancel{2}\eta\left(1+\frac{\eta^2}{6}\right)}\right] = aN\left[\frac{-1}{\eta} + \frac{1}{\eta}\left(1+\frac{\eta^2}{2}\right)\left(1-\frac{\eta^2}{6}\right)\right]$$

$$\simeq aN\left[-\frac{1}{\eta} + \frac{1}{\eta}\left(\cancel{1} + \frac{\eta^2}{3} + O(\eta^4)\right)\right]$$

$$\simeq aN\frac{\eta}{3} \quad\rightarrow\quad \langle z\rangle \simeq \frac{a^2Nf}{3k_BT} \quad\text{or}\quad \boxed{f = \frac{3k_BT}{a^2N}\langle z\rangle}$$

* stiffness (entropic) $= \frac{3k_BT}{a^2N} = \frac{3k_BT}{aL}$ ($L = aN$ contour length) if $\frac{af}{k_BT} \ll 1$ (small force or compression)

• increases as $T\uparrow$, $a\downarrow$ or $L\downarrow$

... FJC

high-force limit $\frac{fa}{kT} \equiv \eta \gg 1$

$$\langle z \rangle = aN \left(-\frac{1}{\eta} + \underbrace{\frac{e^{\eta}+e^{-\eta}}{e^{\eta}-e^{-\eta}}}_{\to 1} \right)$$

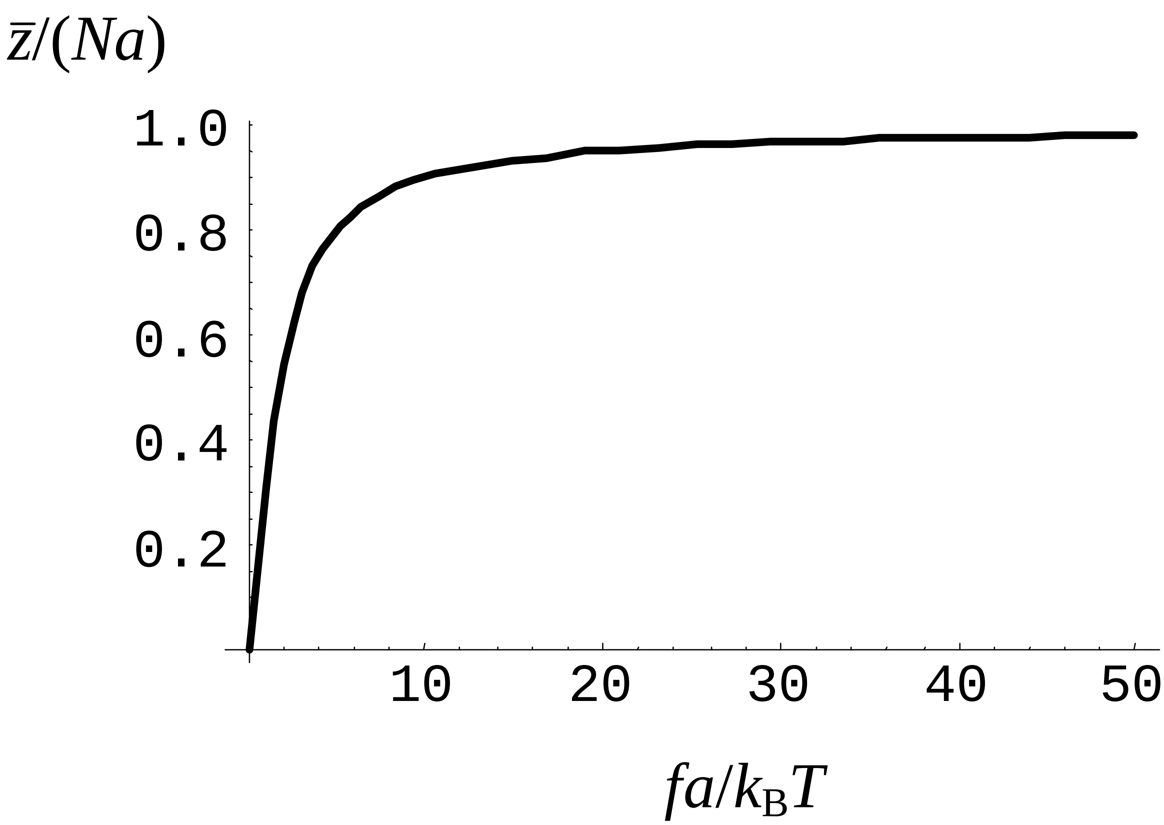
$$\langle z \rangle \simeq aN \left(1 - \frac{1}{\eta} \right)$$

rearranging... $$\frac{fa}{k_B T} = \frac{1}{\underbrace{aN}_{\text{extended length}} - \langle z \rangle}$$

so force to stretch out the chain diverges!

(Note Kleman describes another way to derive the low-force spring constant using random-walk statistics. §15.1)

Freely-Jointed Chain model: avg. length vs. force, *f*



small forces: $f = [3k_BT/(a_2N)]\,\bar{z}$

spring constant

large forces: $fa/k_BT = 1/[Na-\bar{z}]$

(diverges at full extension)

contour length