Introduction

chemical details vs. universal properties

A polymer is a statistical mechanical system, for which the role of entropy is very important
Programme

1. Ideal polymers:
   - conformations: Gaussian coil
   - in an external field
   - in a Self Consistent Field (SCF)

2. Non-ideal polymers
   - excluded volume
   - attractions

3. Concentrated solutions:
   - Flory-Huggins theory
   - scaling theory (semi-dilute solutions)
Polymer conformations

End-to-end vector:

$$\vec{R} = \sum_{i=1}^{N} \vec{r}_i$$

$$\langle \vec{R} \rangle = 0$$
Polymer conformations

End-to-end vector: \[ \vec{R} = \sum_{i=1}^{N} \vec{r}_i \]

\[ \langle \vec{R}^2 \rangle = \langle \vec{R} \cdot \vec{R} \rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle \]

\[ = \sum_{i=1}^{N} \langle \vec{r}_i^2 \rangle + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \langle \vec{r}_i \cdot \vec{r}_j \rangle \]

\[ \propto N \quad \propto N \quad \text{smaller if } |j-i| \text{ larger} \]

\[ \langle \vec{R}^2 \rangle \propto N \]

\[ \sqrt{\langle \vec{R}^2 \rangle} \propto N^{1/2} \]
Chain models (1)

Freely jointed chain:

\[
\langle r_i^2 \rangle = \langle r_i \cdot r_i \rangle = b^2
\]

\[
\langle r_i \cdot r_j \rangle = 0 \quad (i \neq j)
\]

\[
\langle R^2 \rangle = \sum_{i=1}^{N} \langle r_i^2 \rangle + \sum_{i=1}^{N} \sum_{j \neq i} \langle r_i \cdot r_j \rangle = Nb^2 (+ 0)
\]
Chain models (2)

Freely rotating chain:

\[
\langle \vec{r}_i^2 \rangle = \langle \vec{r}_i \cdot \vec{r}_i \rangle = b^2
\]

\[
\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle = b^2 (\cos \theta)^1
\]

\[
\langle \vec{r}_i \cdot \vec{r}_{i+2} \rangle = b^2 (\cos \theta)^2
\]

\[
\langle \vec{r}_i \cdot \vec{r}_j \rangle = b^2 (\cos \theta)^{|j-i|}
\]
Chain models (3)

\[
\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} b^2 \left[ 1 + (\cos \theta)^1 + (\cos \theta)^2 + (\cos \theta)^3 + \cdots \right] = Nb^2 \frac{1 + \cos \theta}{1 - \cos \theta}
\]

\[
= Nb_{\text{eff}}^2 \quad \text{with} \quad b_{\text{eff}} \equiv b \sqrt{\frac{1 + \cos \theta}{1 - \cos \theta}}
\]

General result when NO INTERACTION between segments

\[
\langle \vec{R}^2 \rangle = Nb_{\text{eff}}^2 \quad \text{with more general} \quad b_{\text{eff}}
\]
End-to-end distribution (1)

$P(\vec{R}, N)$: probability of finding $\vec{R}$ after $N$ segments?

Recursion relation:

$$P(\vec{R}, N) = \left( P(\vec{R} - \vec{r}_N, N - 1) \right)_{\vec{r}_N}$$

Taylor expansion ($N \gg 1$ and $\vec{R} \gg \vec{r}_N$):

$$P(\vec{R} - \vec{r}_N, N - 1) \approx P(\vec{R}, N) + \frac{\partial P}{\partial N} (-1) + \sum_{\alpha=x,y,z} \frac{\partial P}{\partial \alpha} (-\vec{r}_{N,\alpha})$$

$$+ \frac{1}{2} \sum_{\alpha=x,y,z} \sum_{\beta=x,y,z} \frac{\partial^2 P}{\partial \alpha \partial \beta} (-\vec{r}_{N,\alpha})(-\vec{r}_{N,\beta}) + \cdots$$
End-to-end distribution (2)

apply $\langle \cdots \rangle_{\vec{r}_N}$:  
$\langle \vec{r}_N \rangle_{\vec{r}_N} = 0$

$\langle \vec{r}_{N\alpha} \vec{r}_{N\beta} \rangle_{\vec{r}_N} = \langle \vec{r}_{N\alpha} \rangle_{\vec{r}_N} \langle \vec{r}_{N\beta} \rangle_{\vec{r}_N} = 0 \quad (\alpha \neq \beta)$

$\langle \vec{r}_{Nx}^2 \rangle_{\vec{r}_N} = \langle \vec{r}_{Ny}^2 \rangle_{\vec{r}_N} = \langle \vec{r}_{Nz}^2 \rangle_{\vec{r}_N} = \frac{1}{3}b^2$
End-to-end distribution (3)

\[ P(\vec{R}, N) \approx P(\vec{R}, N) + \frac{\partial P}{\partial N} (-1) + \frac{1}{6} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) P + \cdots \]

With the definition of the Laplacian \( \Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \)

we thus find that \( P(\vec{R}, N) \) is the solution of:

\[ \frac{\partial P(\vec{R}, N)}{\partial N} = \frac{b^2}{6} \Delta P(\vec{R}, N) \]

cf. the diffusion equation for \( c(\vec{R}, t) \):

\[ \frac{\partial c(\vec{R}, t)}{\partial t} = D \Delta c(\vec{R}, t) \]
End-to-end distribution (4)

Cf. one diffusing colloidal particle (Einstein):

\[ \langle \tilde{R}^2 \rangle = 6Dt \]

An (ideal) polymer is like the **trajectory** of a diffusing particle!
End-to-end distribution (5)

The solution of \( \frac{\partial P(\tilde{R}, N)}{\partial N} = \frac{b^2}{6} \Delta P(\tilde{R}, N) \) is (by analogy):

\[
P(\tilde{R}, N) = \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp \left( -\frac{3\tilde{R}^2}{2Nb^2} \right)
\]
Central Limit Theorem

Consider the sum of $N$ independent, stochastic variables ($N$ is large).
This sum has a normal (= Gaussian) distribution with $\sigma^2 \propto N$.

$$\vec{R} = \sum_{i=1}^{N} \vec{r}_i \quad \Rightarrow \quad \sigma_{\vec{R}}^2 = \langle (\vec{R} - 0)^2 \rangle = \langle \vec{R}^2 \rangle \propto N \left(\times b_{\text{eff}}^2 \right)$$

Variation in $\vec{R}^2$:

$$\sigma_{\vec{R}^2} = \sqrt{\langle (\vec{R}^2 - \langle \vec{R}^2 \rangle)^2 \rangle} = \sqrt{\frac{2}{3}Nb^2}$$

A Gaussian coil is a strongly fluctuating object!

**Conclusion:** many (global) properties of polymers do not depend on the (local) details of the model.
Entropy of a Gaussian coil

\[ S(\vec{R}) = k_B \ln W \]
\[ = \text{cst} + k_B \ln P(\vec{R}) \]
\[ = \text{cst} - \frac{3k_B}{2Nb^2} \vec{R}^2 \]

\[ A(\vec{R}) (= -TS) = \text{cst} + \frac{3k_B T}{2Nb^2} \vec{R}^2 \quad \text{ENTROPIC SPRING} \]
### Conditional probability

**Probability**

\[ P(\vec{R}, N) = G_N(\vec{R} \mid 0) \]

**Conditional probability**

\[ G_N(\vec{R} \mid \vec{R}') \]

**Independent end points:**

\[ G_v(\vec{R}'' \mid \vec{R}') \cdot G_{N-v}(\vec{R} \mid \vec{R}'') \]

**Integrate over** \( R'' \)

\[ \Rightarrow G_N(\vec{R} \mid \vec{R}') \]

**(OK for Gaussian chains)**
Additional polymer models

Gaussian bond model:

Every single bond Gaussian $\propto \exp\left(-\frac{3 \vec{r}_i^2}{2 (1) b^2}\right)$

Bead-spring model:  

spring constant: $\frac{3k_B T}{2(1)b^2}$

(used in the Rouse/Zimm models for polymer dynamics)

Continuous model:

permits the use of path integrals
A polymer in an external field (1)

assume a segment at position $\vec{R}$ has energy $\varphi(\vec{R})$

Taylor expansion:

$$P(\vec{R} - \vec{r}_N, N - 1) \approx \left( P(\vec{R}, N) + \frac{\partial P}{\partial N} (-1) + \cdots \text{etc.} \right) \times \left( 1 - \frac{\varphi(\vec{R})}{k_B T} + \cdots \right)$$

$$\frac{\partial P}{\partial N} = \frac{b^2}{6} \Delta P - \frac{\varphi(\vec{R})}{k_B T} P$$

cf. diffusion in an external field
A polymer in an external field (2)

similarly for the conditional probability $G_N(\vec{R} | \vec{R}')$

\[-\frac{\partial G}{\partial N} = -\frac{b^2}{6} \Delta G + \frac{\varphi(\vec{R})}{k_B T} G\]

$\vec{R}'$ is a parameter, but: $\vec{R} \leftrightarrow \vec{R}'$

cf. $-\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \psi + V(\vec{R})\psi$

QM: time-dependent Schroedinger equation for $\psi(\vec{R}, t)$

linear, partial differential equations; solution method:

separation of variables
Separation of variables

\[ -\frac{\partial G}{\partial N} = -\frac{b^2}{6} \Delta G + \frac{\varphi(\bar{R})}{k_B T} G \]

assume \( G \) can be written as: \( G = f(N)\psi(\bar{R}) \)

\[ -\psi(\bar{R}) \frac{\partial f(N)}{\partial N} = -\frac{b^2}{6} f(N)\Delta \psi(\bar{R}) + \frac{\varphi(\bar{R})}{k_B T} f(N)\psi(\bar{R}) \]

divide by \( f(N)\psi(\bar{R}) \):

\[ -\frac{1}{f(N)} \frac{\partial f(N)}{\partial N} = -\frac{b^2}{6} \frac{\Delta \psi(\bar{R})}{\psi(\bar{R})} + \frac{\varphi(\bar{R})}{k_B T} = \lambda \]

\( f(N) = c \exp(-\lambda N) \)

\[ -\frac{b^2}{6} \Delta \psi(\bar{R}) + \frac{\varphi(\bar{R})}{k_B T} \psi(\bar{R}) = \lambda \psi(\bar{R}) \]

eigenvalue equation \( \Rightarrow \)

eigenvalues \( \lambda_n \), complete set (orthogonal) eigenfunctions \( \psi_n(\bar{R}) \)

\[ G = \psi_n(\bar{R}) \exp(-\lambda_n N) \] or any linear combination for different \( n \)
A polymer in an external field (3)

linear combination: \( G_N (\vec{R} | \vec{R}') = \sum_n c_n \psi_n (\vec{R}) \exp(-\lambda_n N) \)

using \( \vec{R} \leftrightarrow \vec{R}' \)

bilinear expansion: \( G_N (\vec{R} | \vec{R}') = \sum_n \psi_n (\vec{R}) \psi_n (\vec{R}') \exp(-\lambda_n N) \)

where \( -\frac{b^2}{6} \Delta \psi_n (\vec{R}) + \frac{\varphi(\vec{R})}{k_B T} \psi_n (\vec{R}) = \lambda_n \psi_n (\vec{R}) \)

1) continuous spectrum of eigenvalues

example: \( \varphi(\vec{R}) = 0 \quad \Rightarrow \quad \psi_{\vec{k}} = e^{i\vec{k} \cdot \vec{R}} \) and \( \lambda_{\vec{k}} = \frac{1}{6} b^2 k^2 \)

here we need all eigenfunctions \( \Rightarrow \) Gaussian coil
A polymer in an external field (4)

bilinear expansion: \( G_N(\bar{R} | \bar{R}') = \sum_n \psi_n(\bar{R})\psi_n(\bar{R}') \exp(-\lambda_nN) \)

2) discrete spectrum of eigenvalues

\( \Rightarrow \) lowest eigenvalue \( \lambda_0 \) dominates for large \( N \)

GROUND STATE DOMINANCE

\( G_N(\bar{R} | \bar{R}') \sim \psi_0(\bar{R})\psi_0(\bar{R}') \exp(-\lambda_0N) \)

chain ends are decoupled!
A polymer in an external field (5)

segment density $c(\vec{R})$

integrate over: beginning $\nu$

end $\nu$

cf. QM: bound state

$$c(\vec{R}) \sim N |\psi_0(\vec{R})|^2$$
A polymer in an external field (6)

Figure 5. A polymer chain in a spherical cavity of diameter $D$.

An example of this situation is a polymer chain confined to a spherical cavity of diameter $D$ (see figure 5). For this spherical symmetry we can express the Laplacian in terms of the distance to the origin $R$:

$$\Delta \cdots = \frac{1}{R^2} \frac{d^2}{dR^2} (R \cdots)$$

If we now solve equation (2.16) with $\varphi(R) = 0$ within the cavity, but all eigenfunctions $= 0$ outside (since the chain obviously cannot be there), we find as the lowest eigenvalue and (normalized) eigenfunction:

$$\lambda_0 = \frac{2\pi^2 b^2}{3D^2} \quad \text{and} \quad \psi_0 = \frac{1}{R\sqrt{\pi D}} \sin \left( \frac{2\pi R}{D} \right)$$
Lifshitz entropy: derivation  
(for ground-state dominance)

Partition function $Z$: # conformations  
(weighed with Boltzmann factors $\exp(-\varphi(\bar{R}) / k_B T)$)

$$
Z = \int d\bar{R} \int d\bar{R}' G_N (\bar{R} | \bar{R}') \\
G_N (\bar{R} | \bar{R}') \sim \psi_0 (\bar{R}) \psi_0 (\bar{R}') \exp (-\lambda_0 N) \\
Z \sim e^{\lambda_0 N} \left( \int d\bar{R} \, \psi_0 (\bar{R}) \right)^2 \\
end \text{ effects}
$$

free energy:
$$
A = -k_B T \ln Z \sim k_B T \lambda_0 N + \text{end effects}
$$

entropy:
$$
S = \frac{U - A}{T} = \int \frac{1}{T} \varphi(\bar{R}) c(\bar{R}) \, d\bar{R} - k_B \lambda_0 N \\
use \, c(\bar{R}) \sim N \psi_0^2 \\
and \, the \, eigenvalue \, equation \\
and \, eliminate \, \lambda_0
Lifshitz entropy: result

\[ S = N k_B \frac{1}{6} b^2 \int \psi_0(\vec{R}) \Delta \psi_0(\vec{R}) \, d\vec{R} \]

\[ S = -N k_B \frac{1}{6} b^2 \int \left[ \nabla \psi_0(\vec{R}) \right]^2 \, d\vec{R} \quad \text{partial integration using } \Delta \equiv \vec{\nabla} \cdot \vec{\nabla} \]

\[ S = -k_B \frac{1}{24} b^2 \int \frac{\left[ \nabla c(\vec{R}) \right]^2}{c(\vec{R})} \, d\vec{R} \quad \text{using } c(\vec{R}) \sim N \psi_0^2 \]

- independent of \( \varphi(\vec{R}) \)
- also valid for a collection of polymers
- \( S \) decreases because of concentration gradients
- \( S = S[c(\vec{R})] \) (\( S \) is a functional of \( c(\vec{R}) \))
Self-consistent field method

this method incorporates inter-segment interactions:

free energy:

\[ A[c(\bar{R})] = U[c(\bar{R})] - TS[c(\bar{R})] \]

\( U[c(\bar{R})] \) represents e.g. a non-ideal gas of segments

\( c_{eq}(\bar{R}) \) is then obtained by functional minimization

THIS APPROACH NEGLECTS FLUCTUATIONS/CORRELATIONS
Non-ideal polymer chains

\[ U[c(\bar{R})] = N k_B T B c(\bar{R}) \]

\( B \) is the **second virial coefficient** \( (B > 0 \text{ repulsion}) \)

Edwards (1965): \( \langle \bar{R}^2 \rangle \propto N^{6/5} \)

swelling

\[ \text{PURE REPULSION} \]

Total number of configurations (depending on \( R \)) \( \propto \)

\( \propto P(R, N) \propto 4 \pi R^2 \exp \left( -\frac{3R^2}{2Nb^2} \right) \)

but a certain fraction of these configurations is "forbidden":

\[ p(R) \approx \left( 1 - \frac{v_c}{R^3} \right)^{N(N-1)/2} \approx \exp \left( -\frac{N^2 v_c}{2R^3} \right) \]
Non-ideal (repulsive) polymer chains

free energy:

\[
\frac{A(R)}{k_B T} = - \frac{S(R)}{k_B T} = -\ln \left[ p(R) P(R, N) \right]
\]

\[
\approx \text{cst} - 2 \ln R + \frac{3R^2}{2Nb^2} + \frac{N^2 \nu_c}{2R^3}
\]

minimize \( A(R) \) with respect to \( R \)

\( \nu_c = 0 : \quad R_0^* \propto N^{1/2} b \)

\( \nu_c \neq 0 : \quad \left( \frac{R^*}{R_0^*} \right)^5 - \left( \frac{R^*}{R_0^*} \right)^3 \approx \frac{\nu_c}{b^3} N^{1/2} \quad \text{Flory} \)

\( N \gg 1 : \quad R^* \approx R_0^* N^{1/10} \propto N^{3/5} b \quad \text{SWELLING !} \)

RG theory / simulations : \( R^* \propto N^{0.588} b \)
Repulsion combined with attraction (1)

Assumptions:
- only attraction between nearest neighbours
- coordination number: $z$
- solvent-solvent
- solvent-polymer
- polymer-polymer

- random pair contacts:
Repulsion combined with attraction (2)

attractive energy within a coil:

\[ U_{\text{attr}} = N \nu_c c(R) z (\Delta \varepsilon) \]

(\( \nu_c c(R) \) is the probability to find a neighbouring segment)

\[
\frac{U_{\text{attr}}}{k_B T} = -\frac{N^2}{R^3} \nu_c \frac{z \Delta \varepsilon}{k_B T} \quad \text{where} \quad \frac{z \Delta \varepsilon}{k_B T} \equiv \chi \quad \text{(chi-parameter)} \]

\[ \chi \text{ usually } > 0 \]

Compare with repulsive term in \( \frac{A(R)}{k_B T} \), which was: \( \frac{N^2 \nu_c}{2R^3} \)

\[ \nu_c \rightarrow \nu \equiv \nu_c (1 - 2\chi) \]

\[
\left( \frac{R^*}{R_0^*} \right)^5 - \left( \frac{R^*}{R_0^*} \right)^3 \approx \frac{\nu_c}{b^3} (1 - 2\chi) N^{1/2} \quad \text{Flory} \]
Repulsion combined with attraction (3)

\[
\left( \frac{R^*}{R_0^*} \right)^5 - \left( \frac{R^*}{R_0^*} \right)^3 \approx \frac{\nu_c}{b^3} (1 - 2\chi) N^{1/2}
\]

Flory

CONCLUSION:

• at \( \chi = 0 \) swollen chain \( R^* \propto N^{3/5} \)

• at \( \chi = 1/2 \) (\( \theta \)-temperature): ideal chain \( R^* = R_0^* \propto N^{1/2} \)

• right-hand side only small if \( \chi = \frac{1}{2} - \frac{\text{cst}}{\sqrt{N}} \) i.e. abrupt change if \( N \) large

\( \chi > 1/2 \): globule (bound state, cf. QM) \( R^* \propto N^{1/3} \)

• in general \( R^* \sim b N^\nu \)
Repulsion combined with attraction (4)

polystyrene in cyclohexane
Concentrated polymer solutions

\[ c^* \approx \frac{N}{R^3} \approx \frac{N}{(bN^\nu)^3} \approx \frac{\left( N^{-1/2} \leftrightarrow N^{-4/5} \right)}{b^3} \]

very small!

**FLORY-HUGGINS:**

- concentrated systems: \( S(\bar{R}) \) NO
- homogeneous systems: \( S_{\text{Lifshitz}} \) NO
- random mixing (\( \Omega \) places) YES
Flory-Huggins theory (1)

translational entropy: \( S_{tr,sp} \approx -k_B \Omega_{sp} \ln \phi_{sp} \quad (sp = \text{species}) \)

polymer: \( A_{m,p} \approx k_B T \Omega \frac{\phi}{N} \ln \phi \)

solvent: \( A_{m,s} \approx k_B T \Omega (1-\phi) \ln(1-\phi) \)

\[
A_m \approx \Omega k_B T \left[ \frac{1}{N} \phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi \phi (1-\phi) \right]
\]
Flory-Huggins theory (2)

- \( \phi_c = \frac{1}{1+\sqrt{N}} \) (highly) asymmetric

- \( T_c \) follows from \( \chi_c \approx \frac{1}{2} + \frac{1}{\sqrt{N}} \)

  \( T_c \rightarrow \theta \) for large \( N \), i.e. near the coil \( \rightarrow \) globule transition

- note that fluctuations are neglected!
Polystyrene in methylcyclohexane
Scaling theory

- Step length: $b \rightarrow b_g \left( \equiv g^{1/2}b \right)$
- Number: $N \rightarrow N_g \left( \equiv N/g \right)$
- End-to-end distance: $N^{1/2}b \rightarrow N_g^{1/2}b_g \left( = N^{1/2}b \right)$ invariant!
Semi-dilute solution (good solvent)

\[ \phi^* \approx b^3 c^* \approx b^3 \frac{N}{(bN^{3/5})^3} \approx N^{-4/5} \] still very small!

OSMOTIC PRESSURE

DILUTE

\[ \Pi = k_B T \frac{c}{N} \]

SEMI-DILUTE (power law)

\[ \Pi \sim k_B T \frac{c}{N} \left( \frac{\phi}{\phi^*} \right)^m \]

\[ \sim k_B T \frac{c}{N^{1/5}} N^{4/5 \cdot m} \phi^m \]

\[ \Pi \sim k_B T c \phi^{5/4} \sim \frac{k_B T}{b^3} \phi^{9/4} \]

des Cloizeaux

Typical Length Scale

\[ \xi \sim b N^{3/5} \]

\[ \xi = R \]

\[ \xi \sim b N^{3/5} \left( \frac{\phi}{\phi^*} \right)^m \]

\[ \sim b N^{3/5} N^{4/5 \cdot m} \phi^m \]

\[ m = -3/4 \]

de Gennes

\[ \xi \sim b \phi^{-3/4} \]
What is the meaning of ksi? (1)

Flory-Huggins: \[ \Pi \sim \frac{k_B T}{b^3} \phi^2 \sim \frac{k_B T}{b^3} \phi \times \phi \]

des Cloizeaux: \[ \Pi \sim \frac{k_B T}{b^3} \phi^{9/4} \sim \frac{k_B T}{b^3} \phi \times \phi^{5/4} \]

probability of segment \( \times \) probability of contact \( w \)

probability of contact \( w \): lower for scaling theory (correlations!)

Flory-Huggins: \[ \bullet \leftrightarrow \bullet \]

des Cloizeaux: \[ \text{Diagram} \]
What is the meaning of ksi ? (2)

on one chain: number of segments between contacts?

\[ g \text{ monomers: } g \sim w^{-1} \sim \phi^{-5/4} \]
\[ bg^{3/5} \sim b\left(\phi^{-5/4}\right)^{3/5} \sim b\phi^{-3/4} \sim \xi \] distance between chain contacts!

1) volume fraction within one blob:
\[ \frac{gb^3}{\xi^3} \sim \frac{\phi^{-5/4}b^3}{(b\phi^{-3/4})^3} \sim \phi \implies \text{blobs touch!} \]
What is the meaning of ksi? (3)

2) a SEMI-DILUTE SOLUTION is a collection of BLOBS!

\[ \xi \sim b \phi^{-3/4} \]

de Gennes: \( \xi \sim b \phi^{-3/4} \)

3) des Cloizeaux: \( \Pi \sim \frac{k_B T}{b^3} \phi^{9/4} \sim \frac{k_B T}{\xi^3} \) \( \text{blobs are the osmotic units} \)

4) \( \xi \) is also the screening length for the excluded volume

5) \( \phi \to 1: \  \xi(\sim b \phi^{-3/4}) \to b \)

chains in polymer melts are ideal! (Flory)
The diagram illustrates the behavior of polymer solutions in different solvent conditions. It shows the phase diagram with the following key features:

- **X-axis:** Represents concentration or molar fractions.
- **Y-axis:** Represents the number of monomer units or other relevant parameters.
- **Phase Region:** Indicates the two-phase region where the polymer forms distinct phases.
- **Coexistence Curve:** Shows the boundary between single-phase and two-phase regions.
- **Spinodal:** Denotes the critical point where the system becomes unstable.
- **Crossover Line L:** Marks the transition from one phase to another.
- **Theta Line:** Represents the theta conditions where the interaction is minimal.
- **Nearly Ideal Chains:** Indicates the ideal behavior of the polymer chain.
- **Semi-Dilute Solutions:** Depicts the behavior of solutions that are neither too concentrated nor too dilute.

The diagram also highlights various points and regions with specific parameters and conditions, such as:

- *\( \frac{1}{2} \cdot N_A^{-1/2} \):* Represents a critical point for concentration.
- *bN^1/2:* Indicates a parameter related to the number of monomer units.
- *bN^{3/5}:* Another parameter related to the concentration.

The text near the diagram provides additional explanations and conditions for different regions and phases: