Lecture 24: 12.07.05 Flory-Huggins Theory

Today:

Reading:	Dill and Bromberg Ch. 31 ‘Polymer Solutions,’ pp. 593-605.
Supplementary Reading:	

Announcements:

Final quiz:	Tuesday, Dec. 20 1:30pm-4:30pm DuPont Same format and length as first 2 quizzes; you will have 3 hrs but quiz should only take 2 hrs Equation sheet is allowed, as in prior quizzes
Review sessions (tentatively):	Thermo/Stat Mech review: Friday, Dec. 16, 5-7pm (normal recitation room) Structure review: Sunday, Dec. 18, time TBD (normal recitation room)
Thermo coverage on Quiz 3:	lectures 17-24

Last time

Lattice Models of Solutions

- Lattice models are a form of **COARSE GRAINING**, where only the most important molecular details of a system are retained in a statistical mechanical model. This is a powerful approach to create stat mech models where meaningful predictions can be made for complex materials. We began a derivation of the free energy of mixing for a polymer solution based on **Flory-Huggins theory**:

n_p = number polymer chains
N = number of segments per chain
n_s = number of solvent molecules

M = total lattice sites = $n_s + Nn_p$

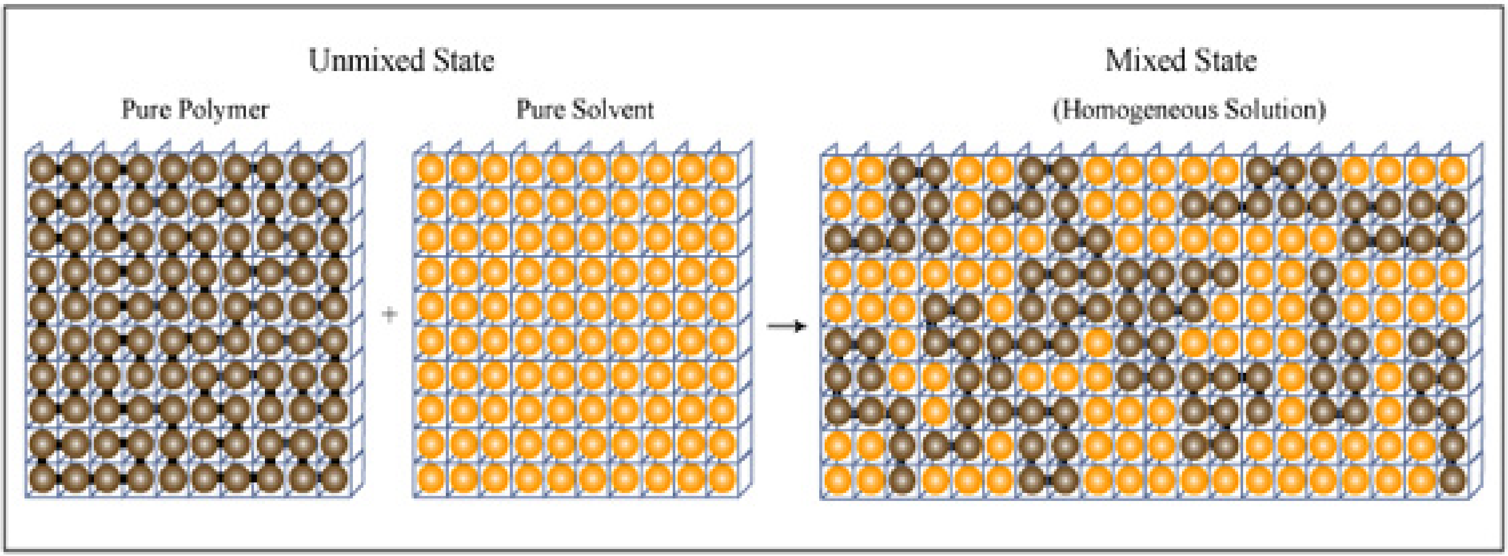


Figure by MIT OCW.

(Dill and Bromberg(1))

volume fraction of polymer:

$$\phi_p = \frac{V_p}{V_p + V_s} = \frac{Nn_p}{M}$$

volume fraction of solvent:

$$\phi_s = \frac{V_s}{V_p + V_s} = \frac{n_s}{M}$$

- **Assumptions:**
  1. Volumes of one solvent molecule and one segment of the polymer chain are equal to one lattice site.
  2. Molecules mix randomly.
  3. Only contribution to possible states are translational configurations ($q = q_{translation}$).
  4. Molecules of a given type are indistinguishable.

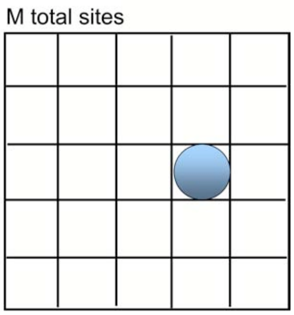
- To predict the thermodynamic behavior of a polymer solution, we want to derive an expression for the free energy of mixing from the molecular states of the system:
  - For a closed system at constant temperature and pressure:

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$$

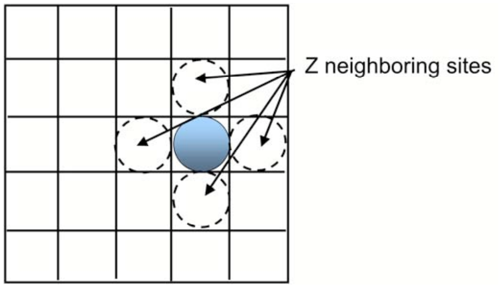
Entropy of mixing in the Flory-Huggins model

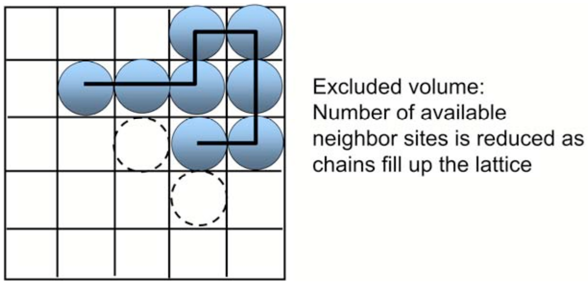
CONFIGURATIONS OF A SINGLE CHAIN

- How do we calculate *W*, the number of uniques states in the polymer system? We start by looking at the number of ways to place a **single polymer chain** on the lattice, $\boldsymbol{\nu}_1$:
    - What are the number of conformations for first bead?

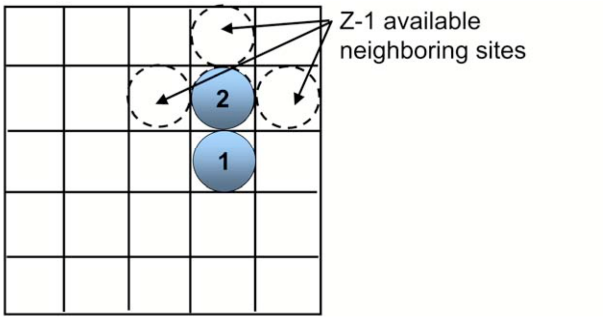


- With the first bead placed on the lattice, what is the number of possible locations for the second segment of the chain?





- Moving on to placement of the third segment of the chain:



- We repeat this process to place all N segments of the chain on the lattice, and arrive at **ν_1, the total number of configurations for a single chain**:

COUNTING CONFIGURATIONS FOR A COLLECTION OF CHAINS

- We can follow the same procedure used for a single chain to obtain the number of configurations possible for an entire set of n_p chains. We start by placing the **FIRST SEGMENT OF ALL n_p CHAINS**. **The number of configurations for the first segment of all n_p chains is ν_{first}**:

$$\nu_{first} = M(M-1)(M-2)(M-3)\cdots(M-(n_p-1)) = \frac{M!}{(M-n_p)!}$$

- The number of configurations for the **(N - 1) remaining segments of all n_p chains is $\nu_{subsequent}$**:

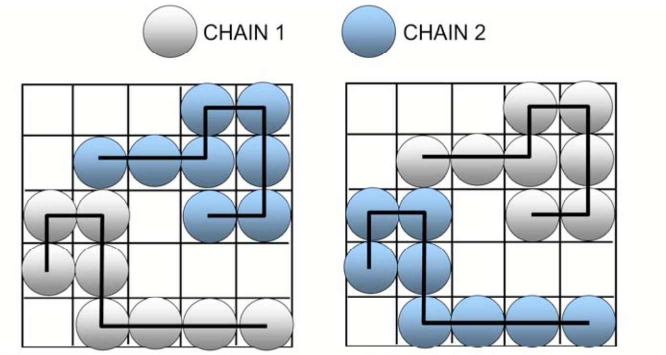
$$\nu_{subsequent} = \left[(z-1)\left(\frac{M-n_p}{M}\right)\right]\left[(z-1)\left(\frac{M-n_p-1}{M}\right)\right]\cdots\left[(z-1)\left(\frac{M-2n_p}{M}\right)\right]\cdots\left[(z-1)\left(\frac{M-N(n_p-1)-(N-1)}{M}\right)\right]$$

$$\nu_{subsequent} = \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{(M-n_p)!}{(M-Nn_p)!}$$

- Putting these two configuration counts together, we have the total number of configurations for the collection of **n_p chains of N segments** each:

$$W = \frac{\nu_{first}\nu_{subsequent}}{n_p!}$$

  - The factor of n_p! Corrects for the over-counting since the polymer chains are indistinguishable, and we can't tell the difference between two configurations with the same polymer distributions but different chain identities:



These two possible configurations are indistinguishable in the system.

- We are now ready to calculate the number of unique states for the unmixed and mixed states:
  - UNMIXED STATE:

PURE SOLVENT:

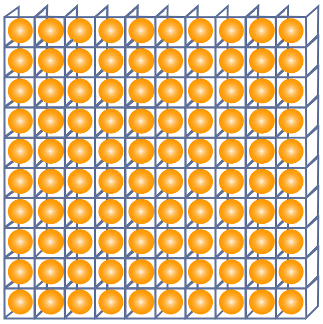
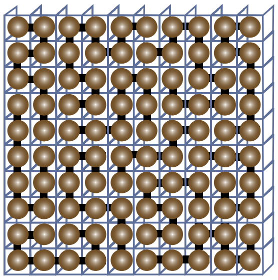


Figure by MIT OCW.

Pure Polymer



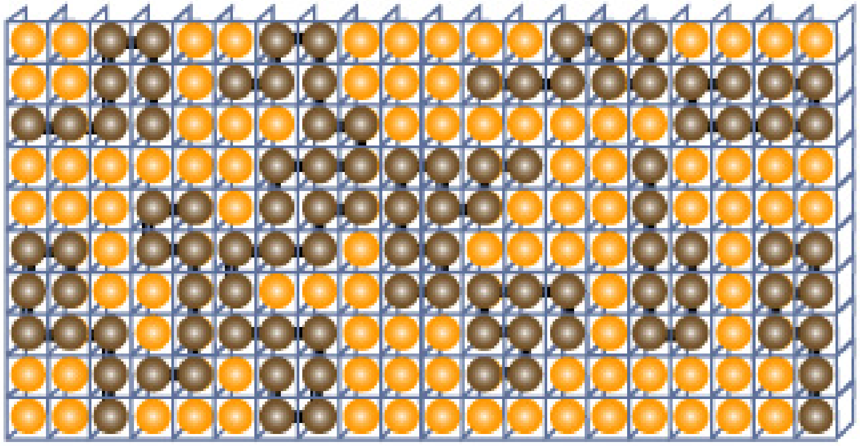
$$Nn_p = M$$

$$W_{\text{pure polymer}} = \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{M!}{\left(M-Nn_p\right)n_p!}$$

$$S^{\text{pure polymer}} = k_b \ln W_{\text{pure polymer}}$$

Figure by MIT OCW.

MIXED STATE:



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$$Nn_p + n_s = M$$

$$W_{solution} = \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{M!}{\left(M-Nn_p\right)n_p!}$$

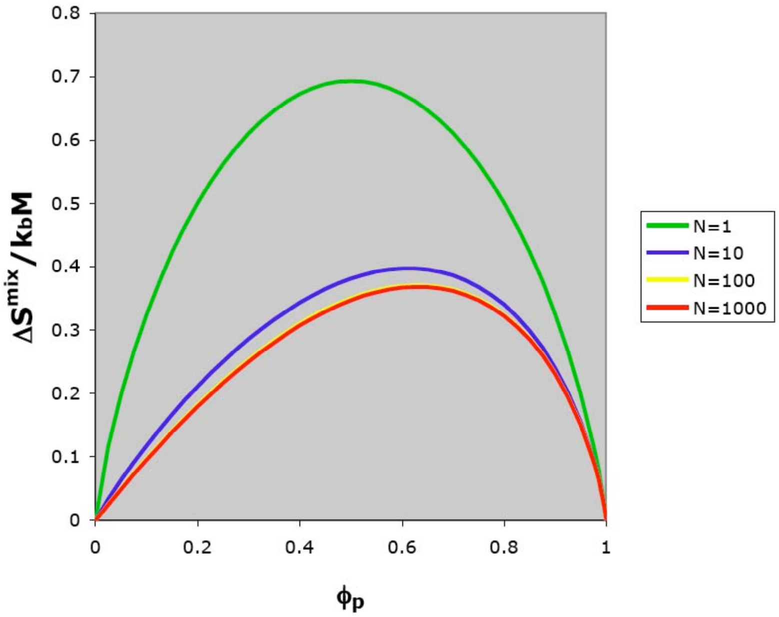
$$\Delta S^{mix} = S^{solution} - S^{unmixed} = S^{solution} - \left(S^{\text{pure solvent}} + S^{\text{pure polymer}}\right) =$$

$$= S^{solution} - S^{\text{pure polymer}}$$

$$= k_b \ln \frac{W_{solution}}{W_{\text{pure polymer}}} = k_b \ln \frac{\left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{M!}{n_s!\,n_p!}}{\left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{(Nn_p)!}{n_p!}} = k_b \ln \left(\frac{Nn_p}{M}\right)^{n_p(N-1)} \frac{M!}{(Nn_p)!\,n_s!}$$

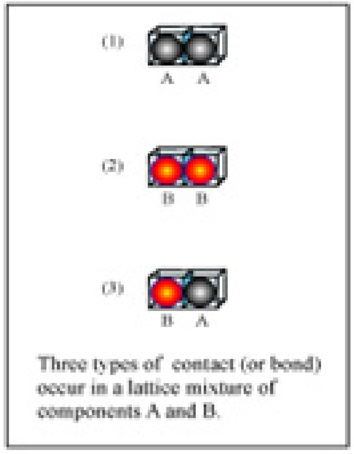
- Applying Stirling's approximation: $\ln x! \approx x \ln x - x$, ...arriving at a final result:

$$\therefore \Delta S^{mix} = -k_b\left[n_s \ln \phi_s + n_p \ln \phi_p\right]$$



The energy of mixing in the Flory-Huggins model

- Molecules form bonds with one another, attract, and repel one another by electrostatic, polar, or Van der Waals interactions- changing the internal energy of the system.



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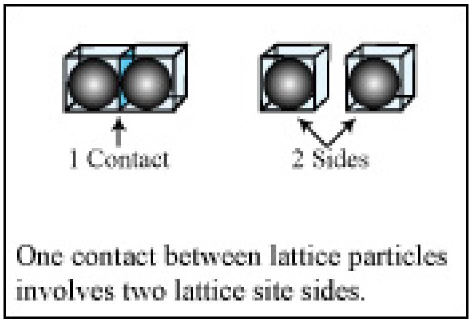


Figure by MIT OCW.

- To account for these interactions in a lattice model, we need to first calculate the enthalpy of mixing. At constant pressure, the enthalpy of mixing will be related to the internal energy of mixing in the following way:

- We will assume in the lattice model that the change of volume on mixing is zero- thus the second term drops out and $\Delta H^{mix} = \Delta U^{mix}$.

- We can directly formulate an expression for the energy of mixing in the model:

- The internal energy of the solution is obtained by considering the contacts between molecules on the lattice:

$$m_{ij} = \#\ \text{i - j contacts}$$

$$\omega_{ij} = \text{energy per i - j contact}$$

$$U^{solution} = \sum (\#\ \text{contacts})\left(\frac{\text{energy}}{\text{contact}}\right)$$

- The total number of contacts made by *polymer segments* or *solvent* molecules on the lattice can be related to the coordination number and the contact numbers m_{ij}:

total solvent contacts:

total polymer contacts:

- Substituting into the expression for the internal energy of the solution, we have:

$$U^{solution} = m_{pp}\omega_{pp} + m_{ss}\omega_{ss} + m_{ps}\omega_{ps}$$

$$U^{solution} = \left(\frac{zNn_p - m_{ps}}{2}\right)\omega_{pp} + \left(\frac{zn_s - m_{ps}}{2}\right)\omega_{BB} + \omega_{ps}m_{ps}$$

$$U^{solution} = \frac{zNn_p}{2}\omega_{pp} + \frac{zn_s}{2}\omega_{BB} + \left(\omega_{ps} - \left(\frac{\omega_{pp} + \omega_{ss}}{2}\right)\right)m_{ps}$$

- The internal energy of the umixed state has a simpler form:

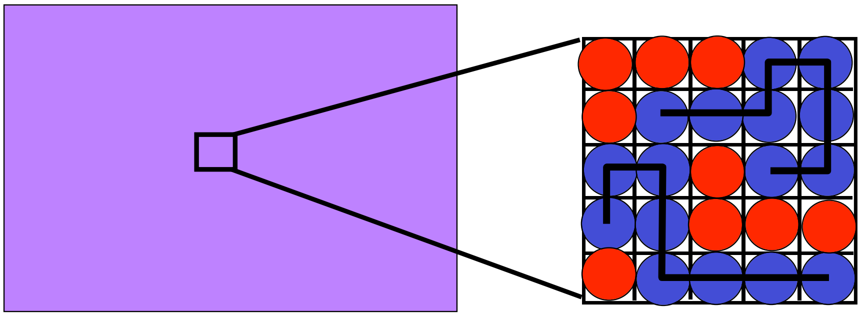
$$U^{unmixed} = (\#\ \text{s - s contacts})\omega_{ss} + (\#\ \text{p - p contacts})\omega_{pp}$$

- This leads us finally to an expression for the energy of mixing:

$$\Delta U^{mix} = U^{solution} - U^{unmixed}$$

The Bragg-Williams approximation

- Our next step is to simplify the last equation- how can we determine m_{ps} from our model?
    - One way to achieve this is to make the approximation that the *polymer* and *solvent* molecules mix randomly on the lattice. In that case, all we need to do to find m_{ps} is calculate the probability of *P-S* contacts for random mixing. This is called the ***mean field approximation*** or the ***Bragg-Williams approximation***. Note that we have already implicitly invoked this approximation in our excluded volume correction in the calculation of the entropy of mixing.



- The probability that a lattice site contains a *polymer segment* is:

- For a single *solvent* molecule, the average number of contacts with polymer segments is then:

- Thus, the total number of P-S contacts is:

- This gives us a completely known expression for the energy of mixing in terms of the interaction energies:

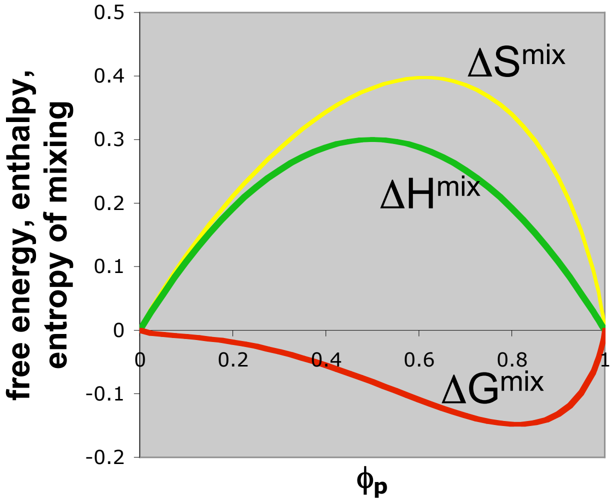
- From this expression, the molar enthalpy of mixing is:

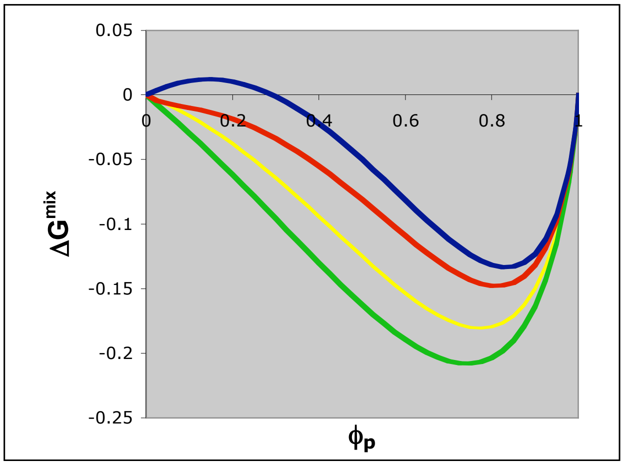
- We define the Flory-Huggins interaction parameter as:
    - χ is a unitless equivalent of Ω, the interaction parameter from the regular solution model. Note that Ω is thus directly related to the molecular energy of interaction between the two components of a binary system!

- The change in internal energy now reduces to:

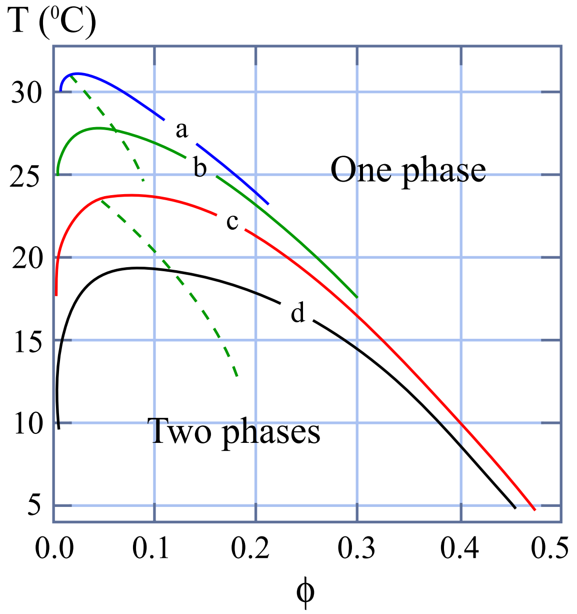
Predictions from the Flory-Huggins model

- Now, this expression, derived directly from our molecule-scale model, can be combined with the lattice model entropy of mixing derived above to provide the free energy of mixing for the regular solution:



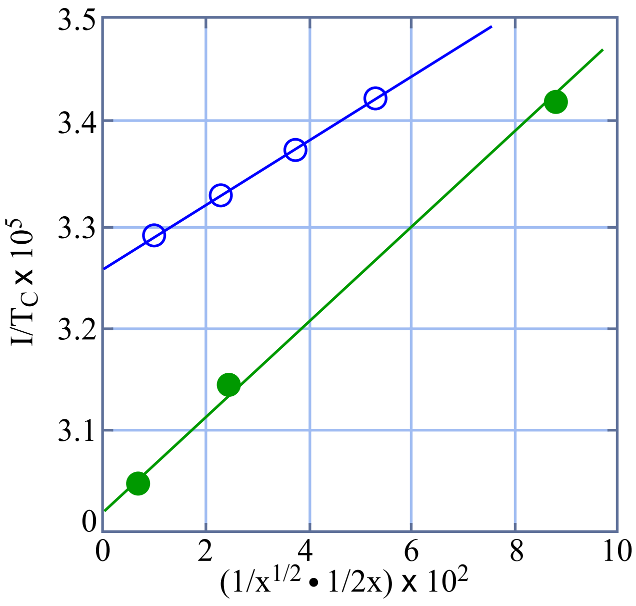


- The Flory-Huggins model predicts major trends in the behavior of real polymer solutions:



Experimental phase diagrams of polystyrene in cyclohexane. Molecular weights (–a–) 1.27 x 10^6, (–b–) 2.5 x 10^5, (–c–) 8.9 x 10^4, (–d–) 4.3 x 10^4. The dashed lines indicate the Flory-Huggins theory predictions for the first and third curves from the top.

Figure by MIT OCW.



A plot of the reciprocal of the critical temperature against the molecular size function for polystyrene fractions in cyclohexane (○) and for polyisobutylene fractions in diisobutyl ketone (●).

Figure by MIT OCW.

- …And this theory is used to predict new behavior in polymers in current research:

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Gonzalez-Leon, Juan, Metin Acar, Ryu, Sang-Woog Ryu, and Ruzette, Anne-Valerie Ruzette, and Anne M. Mayes. "Low-temperature processing of 'baroplastics' by pressure-induced flow." *Nature* 426 (2003): 424-428.

References

1. Dill, K., and S. Bromberg. 2003. *Molecular Driving Forces*, New York.
2. Flory, P. J. 1953. *Principles of Polymer Chemistry*. Cornell University Press, Ithaca.