

POTTS MODEL FOR SOLVENT EFFECTS ON POLYMER CONFORMATION

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Orientational degrees of freedom of polymer subunits can be represented by q -state Potts variables in a lattice theory. As an example, a one-dimensional decorated-lattice model is introduced to describe the effects of a hydrogen-bonding solvent on helix-coil transitions of polypeptides. The results suggest that Potts variables provide a useful representation of highly directional interactions in a variety of systems.

Hydrogen bonding has a central role in the thermodynamic properties of many organic liquids, liquid mixtures [1], and biopolymeric systems [2]. In addition to the anomalous properties of pure (one-component) systems (e.g. the high boiling point of water), these interactions can lead to complicated phase equilibria in the mixtures, and conformational equilibria in polymer solutions.

The essential property of hydrogen bonds which is responsible for phenomena such as certain lower critical solution points [3] and helix-coil transitions [4] is their high directional specificity, and resultant large (negative) entropy of formation. Statistical mechanical lattice models for these systems have been quite successful in describing the thermodynamics and phase transitions, either by putting in the low degeneracy of the bonding state by hand (as in the Zimm-Bragg [5] and other theories [2]), or, more recently, by introducing a statistical variable to represent molecular orientational degrees of freedom [6]. In particular, the coupled Ising-Potts models for lower critical solution points in hydrogen-bonded mixtures, introduced by Walker and Vause [7-10], represent orientations by q -state Potts [11] variables $\sigma = 1, 2, \dots, q$. This is essentially a discretization of orientational phase space, such that $4\pi/q$ is the solid angle of acceptance of the bond. For a realistic description of such interactions, q is of the order of several hundred [8,9]. The Potts model coupling form, $K\delta_{\sigma_i\sigma_j}$ (for nearest neighbors i

and j), embodies the low degeneracy of the bonding state (molecules in the same relative orientation, $\sigma_i = \sigma_j$) relative to the nonbonding states ($\sigma_i \neq \sigma_j$) for $q \gg 1$.

The purpose of this letter is to show, by way of a simple, soluble model, that the use of Potts models to represent orientational degrees of freedom can be extended to hydrogen bonding polymer systems, in which the important orientations are those of the polar groups of the monomer residues. This study was motivated by the striking similarity of so-called "inverted" helix-coil transitions and certain lower critical solution points in binary liquid mixtures [10]: In its conventional form, the helix-coil (hc) transition of a polypeptide is readily understood to result from the competition between configurational entropy, leading to the disordered random coil at high temperatures, and hydrogen bonding energetics, stabilizing the helix at low temperatures. While in many systems the helix is the stable, low temperature configuration, there are some which have inverted transitions, with the helical state at higher T . Of course, at sufficiently high T , the chain again disorders. The original work of Doty and Yang [12] on poly- γ -benzyl-L-glutamate in ethylene dichloride + dichloroacetic acid showed this. The inversion is understood by considering that, in a hydrogen bonding solvent, the heat of desorption of that solvent must be supplied if the amino acid residues are to be free to bond to one another and stabilize the helix [2, 5]. Thus, while the low-temperature chain configura-

tion is helically disordered, the system is highly correlated, through polymer–solvent hydrogen bonds which freeze-out orientational freedom, and lower the total entropy.

Turning now to critical solution points in binary (A + B) liquid mixtures, we see tremendous similarities. The normal transitions are upper critical solution points, explainable in terms of the competition between mixing entropy and interparticle energetics. In many hydrogen-bonded mixtures, lower critical solution temperatures (LCST) are seen, above which the system is phase separated and below which it is homogeneous. As with inverted hc transitions, this low-temperature phase is macroscopically disordered (mixed), but microscopically correlated through A–B hydrogen bonds. The decreased orientational entropy at low temperatures compensates for the increased mixing entropy below the LCST [6–10].

The theory of helix–coil transitions is well developed [4], and inverted transitions have been discussed in the context of other models, particularly by Gibbs and DiMarzio [13]. In the present work, we will see that a natural description of the interplay of the orientational freedom of the monomer residues and nearby solvent molecules is found in the Potts models.

To study the competition between helical ordering and polymer–solvent bonding, I adopt a simplified model of a polymer immersed in a hydrogen-bonding solvent (fig. 1). In actual polypeptides, the primary interactions are between amino acid residues separated by three residues, thus stabilizing the α -helix. These intervening residues give rise to the cooperative nature of the transition [2,4,5], but are not essential to a description of the ordering process: To a first approximation, the polymer consists of independent sublattices within which interaction are between nearest neighbors. The orientational state of each residue i (in particular, the amide group involved in hydrogen bonding) is given by a Potts variable $\sigma_i = 1, 2, \dots, q$. Associated with each site i is a nearby solvent molecule with its own orientational variable $\mu_i = 1, 2, \dots, p$. In general, $q \neq p$ since the residues have a different amount of freedom than the unconstrained solvent molecules [14].

The hamiltonian describing the interactions of these degrees of freedom has two parts:

(i) Adjacent polymer units in the proper relative orientation for hydrogen bonding, represented by $\delta_{\sigma_i \sigma_j}$

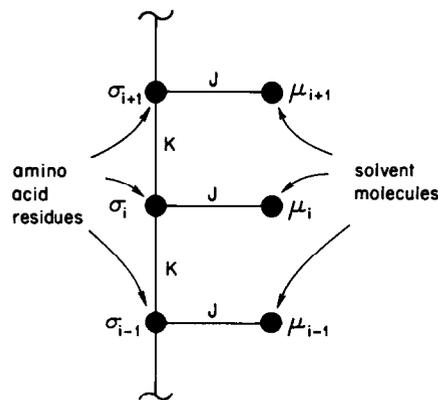


Fig. 1. Topology of interactions of hydrogen-bonding groups along polymer chain with solvent molecules. The variables σ_i and μ_i (i = site label) refer to the orientational state of the amino acid residue amide group and the solvent bonding site, respectively.

= 1, have energy $E_{pp} (< 0)$.

(ii) Polymer units hydrogen bonded to their neighboring solvent molecules, represented by $\delta_{\sigma_i \mu_i} = 1$, have energy $E_{ps} (< 0)$.

This latter interaction, of course, occurs only when the neighboring polymer units are not bonded to each other. Thus, the reduced hamiltonian is ($\beta = 1/k_B T$)

$$-\beta \mathcal{H} = \sum_{\langle ij \rangle} [K \delta_{\sigma_i \sigma_j} + \frac{1}{2} J (1 - \delta_{\sigma_i \sigma_j}) (\delta_{\sigma_i \mu_i} + \delta_{\sigma_j \mu_j})], \quad (1)$$

where the sum is over nearest neighbors i and j on the polymer chain, $K = -\beta E_{pp} (> 0)$, $J = -\beta E_{ps} (> 0)$, and the factor $\frac{1}{2}$ is simply to ensure proper counting. Considering an isolated pair of polymer–solvent bonds is of much lower degeneracy, $q(q-1)$, than that of a polymer–polymer bond plus free solvent, $q(p-1)^2$. As the temperature is lowered, the ordered ground state will be helical (all σ_i equal, μ_i random) if $J/K > 1$, and helically disordered (σ_i random, $\sigma_i = \mu_i$ for all i) if $J/K < 1$. (See refs. [7–10] for the analogous discussion for binary mixture LCSTs). As in the binary mixtures, the different degeneracy scales associated with the two types of bonds establish two temperature scales for the onset of these correlations. Thus, even in a system with $J/K > 1$, substantial helical ordering can occur at intermediate temperatures,

as observed experimentally [4,12].

The model described by eq. (1) is of a class known as "decorated-lattice" models [15], and can be solved exactly in terms of the underlying Potts model of the polymer chain. The partition function is

$$Z(K, J, p, q) = \sum_{\{\sigma_i\}} \sum'_{\{\mu_i\}} \exp[-\beta \mathcal{H}(K, J; \{\sigma_i\}, \{\mu_i\})], \quad (2)$$

where the prime on the sum over solvent orientations excludes the unphysical states of adjacent polymer units bonded together *and* to the solvent. (This exclusion actually produces a very small effect for $p \gg 1$).

The "dedecoration" transformation of summing over solvent orientations can be determined by considering two sites, 1 and 2, say. We write

$$\sum'_{\{\mu_1\}} \exp[K\delta_{\sigma_1\sigma_2} + J(1 - \delta_{\sigma_1\sigma_2})\delta_{\sigma_1\mu_1}] = \exp[K'\delta_{\sigma_1\sigma_2} + \Delta]. \quad (3)$$

Here, K' is the effective coupling between 1 and 2, and Δ is an additive constant in the free energy generated in the dedecoration. Setting $\sigma_1 = \sigma_2$ gives

$$(p-1)e^K = e^{K'+\Delta}. \quad (4)$$

Similarly, when $\sigma_1 \neq \sigma_2$,

$$(p-1) + e^J = e^\Delta. \quad (5)$$

The model has now been mapped onto a single chain N -site Potts model with partition function

$$Z(K, J, p, q) = e^{N\Delta} Z_p(K'(K, J, p, q), q), \quad (6)$$

where Z_p is the q -state Potts partition function. Note that the solvent degrees of freedom have served simply to introduce a non-trivial relationship between the actual temperature of the system (here chosen to be $T = 1/K$) and the temperature as measured by the effective polymer-polymer coupling K' . The analogous result was obtained in the work on binary mixtures, where the underlying model has Ising variables (A, B) instead of Potts variables [7-10].

The properties of the Potts model are easily determined from the eigenvalues of the associated transfer matrix; $\lambda_> = e^{K'} + q - 1$, $\lambda_< = e^{K'} - 1$, where $\lambda_>$ is the larger. In the limit of long chains, where $(\lambda_</\lambda_>)^N \ll 1$, the reduced free energy $f = N^{-1} \ln Z$ is

$$f = \Delta + \ln(e^{K'} + q - 1). \quad (7)$$

The quantity of most relevance to experiments is the fractional helicity θ , which is probed by optical rotation studies [4]. From eqs. (1), (4), (5) and (7),

$$\begin{aligned} \theta &= N^{-1} \left\langle \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j} \right\rangle = \partial f / \partial K \\ &= \partial \Delta / \partial K + [1 + (q-1)e^{-K'}]^{-1} \partial K' / \partial K \\ &= [1 + (q-1)[e^{-K} + (p-1)^{-1}e^{J-K}]]^{-1}. \end{aligned} \quad (8)$$

The competition between the two types of order, polymer-polymer (helical) and polymer-solvent, is now apparent. As temperature T drops ($K, J \rightarrow +\infty$), $\theta \rightarrow 1$ (0) for $J < (>) K$. While there can be no long-range order in this one-dimensional system in the absence of long-range interactions, we may distinguish the ordered and disordered polymer chains based on a reasonable choice for θ ($0 \leq \theta \leq 1$). The temperature variation of the helicity is shown in fig. 2 for various values of the competition parameter $\alpha = J/K$. The orientational parameters q and p were set at 50 and 500 respectively, to represent the different scales of

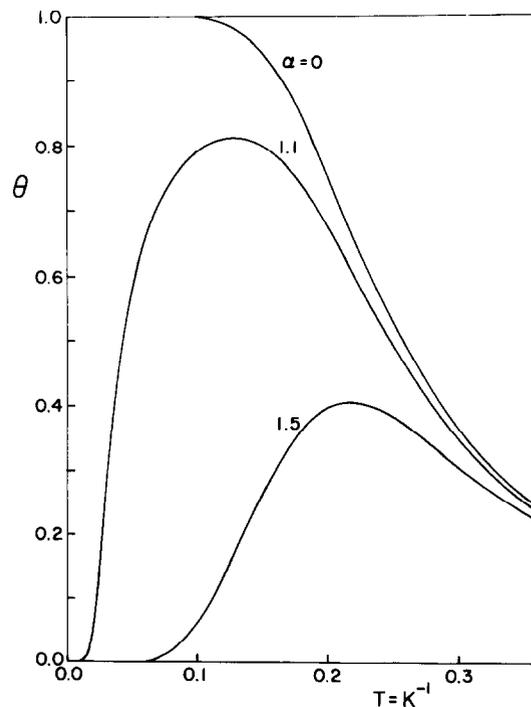


Fig. 2. Helicity as a function of temperature from eq. (8) with $q = 50$, $p = 500$ and several values of J/K , as indicated.

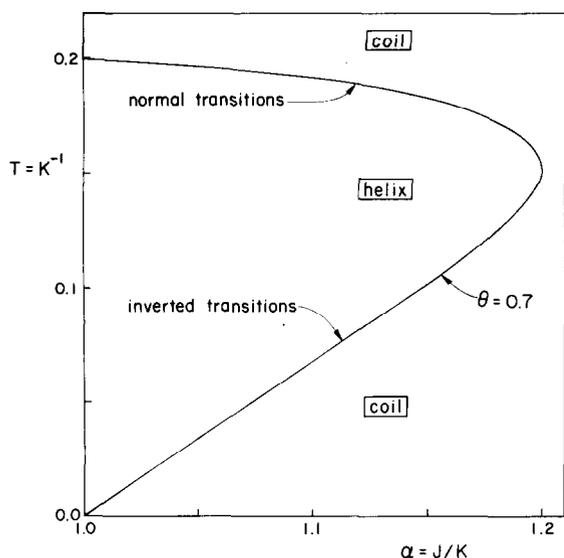


Fig. 3. Temperatures at which the helicity equals 0.7 as a function of the competition parameter $\alpha = J/K$ for $q = 50$, $p = 500$. The high-temperature "coil" state is totally disordered, while the low-temperature "coil" state is helically disordered, but correlated through polymer-solvent hydrogen bonds.

orientational freedom of the residues and solvent molecules^{#1}. Note the dramatic temperature dependence of θ in the vicinity of the lower transition ($\alpha = 1.1$), as seen in experiments. The rather gradual decrease in θ at the normal transition is a consequence of the low directionality chosen for the residue-residue interactions. It is easy to show that the temperature derivative of the θ - T curve scales like $[\ln(q-1)]^2$ at the $\theta = 1/2$ point. Fig. 3 shows the temperatures at which $\theta = 0.7$ (meaning a significantly helical chain) as a function of α , for $\alpha \geq 1$. In this range, there are two "ordering" temperatures, the lower being the inverted transition. These results are very similar to those from the work on binary mixtures, in which closed-loop coexistence curves come and go as a function of a competition parameter (see fig. 19 of ref. [8]).

The inclusion of further-neighbor interactions, necessary for a description of the cooperativity of the transition, can be formulated in the context of the hamiltonian of eq. (1), although the mathematics becomes quite complicated. A simpler, self-consistent formulation can be described as follows: As the sub-

^{#1} For a related discussion of these ideas, see ref. [14].

lattices order, the free polymer sites between bonded segments lose orientational freedom because of the geometrical constraints of the latter sites. Thus, the entropy lost when they do form a hydrogen bond is less than if they did so from within a totally disordered chain, while the energy of such a bond is changed little. Therefore, the effective q of the segments decreases with increasing overall helicity. Within a given sublattice, this can be approximated by a self-consistent q of the form, say, $q = q_0 - q_1\theta$, where $-k_B \ln(q_0 - q_1 - 1)$ is the entropy of formation of a hydrogen bond between residues constrained by a fully ordered chain [9], and q_0 reflects the directional freedom in the disordered chain. Substituting such an expression into the order parameter of a simple one-dimensional Potts model, and solving for the self-consistent θ , one finds that as the cooperativity parameter q_1/q_0 increases toward unity, the sharpness of the helix-coil transition increases.

In summary, we see that an extremely simple representation of directional interactions in polymer systems is achieved through the use of Potts variables to describe molecular orientations. The parameters of the theory can be related to physical quantities such as the energy and entropy of formation of the hydrogen bonds, as in the analogous work on binary mixtures [9]. This type of model is also currently being studied in the context of liquid crystal transitions in polymeric systems, in which conformational changes of the molecules can drive liquid crystalline phase transitions [14]. The inclusion of entropic effects through the use of q -state Potts spins may also prove useful in other problems of polymer conformation, for which the Ising model is too restrictive. Possible applications include the study of both static and dynamic properties.

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