Role of Long-Wavelength Degrees of Freedom in the Rod-to-Coil Transition in Polymers

Nigel Goldenfeld

Institute for Theoretical Physics, University of California at Santa Barbara, Santa Barbara, California 93106

and

J. W. Halley

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

We present a model of the rod-to-coil transformation in a single-stranded polymer which includes the effects of long-wavelength degrees of freedom in the straight parts of the chain. The model exhibits a true first-order phase transition in qualitative agreement with the results of an experiment.

PACS numbers: 64.60.Cn, 36.20.Ey

Recently there has been renewed interest in the conformations of polymers in dilute solution. The discovery during the 1960's that some polymers exhibit a sharp conformational transformation from a straight, rodlike configuration to a random coil when the temperature or pH of the solvent is varied prompted a variety of attempts to find a description in terms of one-dimensional statistical mechanical models.[1,2] Whereas these theories predict a true phase transition only for double-stranded polymers, a recent Letter[3] reports the observation of a sharp rod-to-coil transformation in a single-stranded polymer.

The purpose of this Letter is to suggest that rod-to-coil transformations in single-stranded polymers can actually be very close to being true phase transitions. We show that long-wavelength degrees of freedom in the polymer effectively induce long-range interactions in the molecule, leading to a first-order phase transition. Previous theoretical treatments of the transformation have neglected these degrees of freedom, but they have recently attracted experimental attention.[4,5] Our mechanism for the single-stranded polymer leads to a phenomenology for the single chain which is similar to that of Poland and Scheraga[1] for the double-stranded polymer.

The basic assumption of our calculation and earlier work is that the partition function for a single polymer takes the form

$$Z_N = \sum_{q=1}^{\infty} \sum_{\{i_\sigma, j_\sigma\}} \prod_{\sigma=1}^{q} (u_{i_\sigma} v_{j_\sigma}),$$ (1)

where the chain is described by rod sections (actually extended helices in polyamino acids and nucleic acids) of integer lengths $i_1, i_2, i_3, \ldots$, separated by coiled sections of lengths $j_1, j_2, j_3, \ldots$. In (1), the sum respects the constraint that the total number N of repeat units in the chain is

$$N = \sum_{\sigma=1}^{q} (i_\sigma + j_\sigma).$$

The free energies of a rod section of length i_σ and a coil section of length j_σ are respectively $-k_B T \ln u_{i_\sigma}$ and $-k_B T \ln v_{j_\sigma}$; we picture the coiled state as consisting of a condensation of j_σ consecutive monomers in a "kinked" (gauche or *cis*) conformation and the rod state as i_σ monomers in the straight (*trans*) conformation. In this well-known model there is no energetic interaction between the straight and disordered parts of the chain. In the model for the phonon degrees of freedom of the chain introduced below within the framework of Eq. (1), this means that there is no transmission of phonons from the ordered to the disordered parts of a chain. There is some numerical evidence that, at least for some detailed harmonic models, this is quite a good approximation.[6] It is very likely that this feature of the model is essential for the existence of the sharp phase transition which we find. In the first part of this Letter we present a plausibility argument of the Landau[7] type which suggests that a long-range ordered state is possible at low temperatures if u_{i_σ} and v_{j_σ} are of the form

$$-\ln u_{i_\sigma} = -a i_\sigma + b + c \ln i_\sigma,$$ (2a)

$$-\ln v_{j_\sigma} = -j_\sigma \ln \omega,$$ (2b)

where a, b, and c, and ω are real functions of the temperature, independent of i_σ and j_σ. The Landau argument suggests that a phase transition will occur if $c > 1$. In the second part of this Letter we sketch a derivation of (2) from a microscopic model of the phonon degrees of freedom of the polymer, and prove rigorously that the model exhibits a phase transition at a nonzero temperature, whenever c is larger than 1. In particular, our model gives $c = 3$ and predicts a first-order phase transition. If we were to interpret $-\ln u_{i_\sigma}$ as the free energy of coiled sections (rather than of straight sections as we do here) and $-\ln v_{j_\sigma}$ as the free energy of straight sections, then the same form (2) would arise in the model of Poland and Scheraga which takes account of the entropy of loops in double-stranded polymers but not of phonon degrees

of freedom.

Landau argument.—Consider the free energy of a of length N, broken by a single "kink" at any point between the ϵNth and the $(1-\epsilon)N$th monomer. ϵ is a small arbitrary cutoff, independent of N. If the chemical potential of a kink is Δ then the free energy F_N' of all such configurations is given by

$$e^{-\beta F_N'} = e^{-\Delta\beta} \int_{\epsilon N}^{(1-\epsilon)N} dS \exp[-\beta(F_S + F_{N-S})], \quad (3)$$

where F_S is the free energy of a straight chain of length S. Evaluating the integral we find

$$F_N' = \Delta + k_B T \Omega_\epsilon(c) + k_B T(-aN + 2b + 2c\ln N), \quad (4)$$

where

$$\Omega_\epsilon = \int_\epsilon^{(1-\epsilon)} dx/[x(1-x)]^c.$$

Thus

$$F_N' - F_N \xrightarrow[N\to\infty]{} (c-1)k_B T \ln N, \quad (5)$$

demonstrating that for $c > 1$ an ordered rod phase with no kinks at all is thermodynamically stable at low temperatures.

$$a = \sum_\nu (k_B T/hB_\nu)^{1/m_\nu}(2d/\pi) \int_0^\infty [x^{1/m_\nu}/(e^x - 1)]dx,$$

$$b = \sum_\nu \{ -m_\nu[1 + 1/2\ln(\pi/2d)] - \tfrac{1}{2}\ln(hB_\nu/k_B T)\},$$

In obtaining these expressions we have assumed that $k_B T \ll h\omega_0$, where ω_0 is the largest frequency for which $D(\omega) = \sum_\nu \delta(\omega - \omega_\nu)$, and we have used the lowest order Euler-Maclaurin expansion[9] as well as an integration by parts to isolate the infrared singularity which gives rise to the expression for c in (7). d is the distance between monomers along the chain. We will also need the following expressions for a and b in the opposite limit that $k_B T \gg h\omega_{max}$, where ω_{max} ($> \omega_0$) is the largest frequency for which $D(\omega)$ is nonzero:

$$a \xrightarrow[h\omega_{max} \ll k_B T]{} 3p \ln(h\omega_{max}/k_B T),$$

$$b \xrightarrow[h\omega_{max} \ll k_B T]{} -3p \ln(h\omega_{max}/k_B T), \quad (8)$$

in which $3p$ is the total number of degrees of freedom per monomer. c in this limit retains the value given in (7).

Coil free energy.—The free energy $-k_B T \ln v_{j_\sigma}$ of a coil section of length j_σ in our model has three parts: The first is the energy Δ required to form each of the j_σ kinks. The second part arises from the entropy of a random walk of j_σ steps. We will ignore self-avoiding effects for simplicity of presentation only and estimate the random-walk free energy by restricting the walk to a lattice with coordination number z. Finally, in the high-temperature limit, it is necessary to take account

Rod free energy.—We now proceed to discuss the de-details of the physics which give rise to (2) in our model. The long-wavelength vibrational modes of a rigid straight rod are well known[8] to be a longitudinal mode and a torsional mode, each with frequencies proportional to the wave vector k, and two transverse or bending modes, each with frequencies proportional to the square of the wave vector. Thus we can write the density $D(\omega)$ of vibrational states of the rod at low frequencies as $D(\omega) = \sum_\nu^{\nu=4}\delta(\omega - \omega_\nu)$, in which $\omega_\nu = B_\nu k^{m_\nu}$. Here $m_\nu = (1,1,2,2)$ and B_ν are constants. With use of this form, the vibrational free energy at low temperatures of a rod i_σ monomer units long can be evaluated from the general form

$$\beta F_{i_\sigma}^{rod} = -\ln u_{i_\sigma} = \int d\omega\, D(\omega)\ln(1 - e^{-\beta h\omega}). \quad (6)$$

Here we omit a temperature-independent term arising from zero-point motion which has no effect on our results. The effects that we consider are essentially classical and the only role of quantum mechanics here is in providing cutoffs at high frequencies. [In the systems of interest, the classical approximation to the integral in Eq. (6) is not valid for the entire spectrum.] Equation (6) gives equation (2a) with

$$c = \sum_\nu m_\nu/2. \quad (7)$$

of the vibrational modes of coiled parts of the chain. We will assume on the basis[9] of analytical and numerical studies of the vibrational modes of coiled chains that vibrational modes make a negligible contribution to the coil free energy at low temperatures because the frequency spectrum is essentially bounded from below. Though the conclusions of Ref. 9 depend on some features of the harmonic model used, we can show that other reasonable harmonic models do not change our qualitative conclusions. With these assumptions we find equation (2b) with

$$w = e^{(-\Delta\beta + \ln z)} \quad (9)$$

at low temperatures, and with

$$w = (k_B T/h\omega_{max}')^{3p} \quad (10)$$

at high temperatures. Here ω_{max}' is an upper limit to the vibrational spectrum of the coil.

Phase transitions.—We turn now to the calculation of the thermodynamic behavior, which is performed by use of the generating functions[1,2,10]

$$U(x) = \sum_{n=1}^\infty u_n x^{-n} = e^{-b}\sum_{n=1}^\infty \left(\frac{e^a}{x}\right)^n \frac{1}{n^c},$$

$$V(x) = \sum_{n=1}^\infty v_n x^{-n} = w/(x - w). \quad (11)$$

$U(x)$ is convergent for $x > e^a$. For $c \leq 1$, $U(e^a)$ is divergent. For $1 < c \leq 2$, $U(e^a)$ is convergent but $[dU/dx]_{e^a}$ diverges, while for $c > 2$, both $U(x)$ and dU/dx diverge at $x = e^a$. Lifson[10] has shown (see also Ref. 2) that the partition function Z_N is the largest root of

$$U(x) - 1/V(x) = 0, \tag{12}$$

so that a nonanalyticity can arise in the free energy when $x = e^a$. This is shown in Fig. 1, where the features of a graphical solution of (12) are illustrated. (The following discussion of the phase transition is similar to that found in Refs. 2 and 10 but, because our model is physically different, the temperature dependence of U and V is different.) As the temperatures rises from $T = 0$, the line $y = V^{-1}(x)$ pivots in a clockwise direction about $x = 0$, $y = -1$. In Fig. 1(a) (for $c \leq 1$), the point of intersection of $y = V^{-1}(x)$ and $y = U(x)$ moves continuously to the right at T increases, and there is no nonanalytic behavior in Z_N. In Figs. 1(b) and 1(c), the point of intersection begins to move only when T is sufficiently large. The discontinuity in slope and the value, respectively, of $U(x)$ give rise to a continuous phase transition in the case $1 < c \leq 2$ [Fig. 1(b)] and to a first-order transition in the case $c > 2$ [Fig. 1(c)]. These results are consistent with the Landau argument presented above. In the

case of interest here, $c = 3$, and so we expect the transition to be first order. (The critical exponents for the case $1 < c \leq 2$ have been calculated previously.[2,11]) The order parameter may be taken to be the fraction of monomers in the rod phase and changes discontinuously across the transition.

It remains to show that our model gives rise to a phase transition given the specific temperature dependence of the parameters a, b, and w given in Eqs. (7)–(10). The condition $U(e^a) = V^{-1}(e^a)$ implies that the transition temperature is given by the solution to the equation

$$f(T_c) = e^a/w - 1 - e^{-b}\zeta(c) = 0, \tag{13}$$

where ζ is Riemann's zeta function. By use of Eqs. (7)–(10) we establish that the high- and low-temperature limits of the function $f(T)$ are

$$f(T) \rightarrow \begin{cases} (1/z)e^{\Delta/k_B T}, & k_B T \ll \hbar\omega_{max}, \\ (1/z)(\omega'_{max}/\omega_{max})^{3p} - 1, & k_B T \gg \hbar\omega_{max}. \end{cases} \tag{14}$$

The low-temperature limit is strongly positive, while the high-temperature limit is negative as long as the condition

$$(\omega'_{max}/\omega_{max})^{3p} < z \tag{15}$$

is satisfied. Thus, under the condition (15) there will be at least one solution to (13) and a phase transition from a low-temperature phase with no coiled parts to a high-temperature coiled phase. z is expected to be of the order of 10 and ω'_{max} and ω_{max} are of the same order (as expected on physical grounds and confirmed by numerical simulations). Thus the condition (15) can be expected to be satisfied in realistic situations. The argument does not exclude several transitions, but unless $D(\omega)$ is unexpectedly singular at finite frequencies we do not anticipate them. To exclude multiple transitions rigorously requires a detailed model of the density of states at all frequencies which we do not formulate here.

Solvent effects and experiment.—The experiments[3,12] mentioned in the introduction were performed on polymers in dilute solution, while our theory is formulated for an isolated chain. We argue here that the theory can in fact be applied to a chain in solution as long as the low-lying modes of the chain which give rise to the infrared singularity associated with the term $c \ln i_\sigma$ in (2a) are slower than any modes of the solvent. If this is the case, then the solvent will act as a Gaussian white-noise source on the polymer and will cause it to relax to an equilibrium distribution characteristic of the short-range interactions between the polymer monomers alone. Thus our equilibrium theory
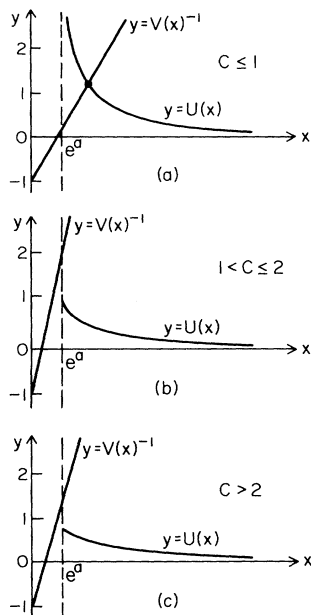

FIG. 1. Illustration of graphical solution to Eq. (12). As the temperature is varied, the intersection of $y = U(x)$ and $y = V(x)^{-1}$ traces out the partition function. Depending on the nature of the singularity in $U(x)$ at $x = e^a$, three behaviors can occur: (a) $c \leq 1$, no phase transition; (b) $1 \leq c \leq 2$, continuous transition; or (c) $c > 2$, first-order transition.

for the isolated chain can be applied. Such an argument can be put on a more precise basis by deriving a Langevin equation for the slow degrees of freedom of the polymer-solvent system.[13] Under these conditions the modes are actually overdamped but still provide an effective coupling between the coiled parts of the chain and the same conclusions follow. If the transition were second order, then the transverse modes of the chain would always be slower than any modes of the liquid if one were close enough to the transition, because the transverse-mode frequencies go as the wave vector squared while the acoustic-mode frequencies of the three-dimensional solvent are linear in the wave vector. In the case of a first-order transition, one can only be sure that the low-lying modes of the chain are lower than any solvent frequencies if the mass of a monomer is much larger than the mass of a solvent molecule. If the acoustic and torsional modes are not obeying the required conditions but the transverse modes are, then the structure of the theory will not change essentially except that the value of c will change from 3 to 2, giving rise to a transition which is at the border between first and second order. We have not studied this interesting possibility, which is suggestive of tricritical phenomena.

In the experiments of Heeger and co-workers[3,12] we note that some reported features do appear to suggest the first-order transition which we predict. In particular, the light-scattering data[3] seem to indicate a very sharp change from rod to coil, and hysteresis and very slow kinetics are reported in several of the optical-absorption studies of the transition.[12] Our model incorporates only features which apply quite generally to a wide class of polymers and we can therefore anticipate that similar transformations may occur in other dilute solutions of natural and synthetic polymers.

[1]D. Poland and H. Scheraga, *Theory of Helix-Coil Transitions in Biopolymers* (Academic, New York, 1970).

[2]F. Weigel, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, New York, 1983), Vol. 7, pp. 101–147.

[3]K. C. Lim, C. R. Fincher, and A. J. Heeger, Phys. Rev. Lett. **50**, 1934 (1983).

[4]G. S. Edwards, C. C. Davis, J. D. Saffer, and M. I. Swicord, Phys. Rev. Lett. **53**, 1284 (1984).

[5]S. M. Lindsay, J. W. Powell, and A. Rupprecht, Phys. Rev. Lett. **3**, 1853 (1984).

[6]J. W. Halley, J. Onffroy, M. Thorpe, and A. Walker, Phys. Rev. B (to be published).

[7]L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, Reading, Mass. 1958), p. 482.

[8]L. D. Landau and E. M. Lifschitz, *Theory of Elasticity* (Pergamon, New York, 1970), pp. 113–117; see also W. N. Mei, M. Kohli, E. W. Prohofsky, and L. L. Van Zandt, Biopolymers **20**, 833 (1981); a somewhat similar study by A. Peterlin and E. W. Fischer, Z. Phys. **159**, 272 (1960), included only the longitudinal mode.

[9]H. and B. S. Jeffries, *Mathematical Physics* (Cambridge Univ. Press, Cambridge, Mass., 1966), p. 279.

[10]S. Lifson, J. Chem. Phys. **40**, 3705 (1964).

[11]M. Ya. Azbel, Biopolymers **19**, 95 (1980), and Phys. Rev. A **20**, 1671 (1979).

[12]K. C. Lim and A. J. Heeger, unpublished.

[13]G. F. Mazenko, in *Correlation Functions and Quasiparticle Interactions in Condensed Matter*, edited by J. W. Halley (Plenum, New York, 1977), pp. 152–166.