

Scaling near the θ point for isolated polymers in solution

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Recently questions have been raised as to the conclusions that can be drawn from currently proposed scaling theory for a single polymer in various types of solution in two and three dimensions. Here we summarize the crossover theory predicted for low dimensions and clarify the scaling arguments that relate thermal exponents for quantities on approaching the θ point from low temperatures to those associated with the asymptotics in polymer length at the θ point itself.

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Recently some interesting work has been completed on stretched polymers in a poor solvent by Grassberger and Hsu [1] (GH) and on collapsed polymers on a cylinder by Hsu and Grassberger [2] (HG). In the course of these works various scaling conjectures were discussed; the question arose as to whether they can be derived from theory currently in the literature. It is therefore timely to revisit questions such as these: we not only address the questions raised in (GH) and (HG), but discuss how such questions can be answered in general.

The basic framework of the polymer problem has been, and still is, given by the seminal works of de Gennes and Duplantier [3–5] which describe the long length behavior in terms of critical phenomena. Hence the basic properties of such polymers are argued to display scaling behavior. Much work has been subsequently done to verify specific scaling predictions in both two and three dimensions (for examples, from the past 10 years see Refs. [1,2,6–10]). More generally, scaling usually imposes certain relationships between critical exponents (a review of the more general scaling framework can be found in Ref. [11]—see also Ref. [12]) and it is these relationships that are addressed here.

Of particular interest here is the scaling of quantities on approaching the θ point from the collapsed phase. The collapsed phase itself has received attention relatively recently [1,2,13,14]. Much less is known here, partially because the long length behavior is no longer a critical phenomenon. This is in contrast to the swollen phase and the transition point, which are both critical. To make clear the answers to questions such as those raised in GH and HG it is first timely to restate, in compact fashion, the conjectured crossover scaling theory for a single polymer between good and poor solvents (high and low temperatures respectively), and then demonstrate how questions such as those raised can be answered in general.

As temperature gets decreased, an isolated polymer in solution undergoes a phase transition from a swollen coil to a collapsed globule via a critical θ state at a temperature T_θ .

The standard description of this polymer collapse transition is a tricritical point related to the $n \rightarrow 0$ limit of the $(\phi^2)^2 - (\phi^2)^3 O(n)$ field theory [3–5]. Scaling theory can therefore be derived, in principle, from this tricriticality [15]. The upper critical dimension for the swollen state is four while for the θ state it is expected to be three. As confluent logarithmic corrections complicate the discussion in three dimensions, the crossover theory should be cleanest for dimensions strictly below the upper critical dimension. Let us therefore concentrate our discussions on two dimensions.

Consider now, for simplicity, some quantity $Q(T, N)$, associated with a property of the polymer, that is a function of the length N and the temperature T of the polymer. Moreover, let it be a quantity that has an algebraic asymptotic behavior for large N at any fixed value of T , such as the radius of gyration $R_g(T, N)$, for example. Such a quantity would then be expected to possess three different behaviors: For fixed $T > T_\theta$,

$$Q(T, N) \sim a_+(T)N^{q_+}, \quad (1)$$

for $T < T_\theta$,

$$Q(T, N) \sim a_-(T)N^{q_-}, \quad (2)$$

while for $T = T_\theta$,

$$Q(T, N) \sim a_\theta N^{q_\theta}, \quad (3)$$

each as $N \rightarrow \infty$. The assumption of crossover scaling [15–17] applied to this system [11] implies that there exists a crossover exponent ϕ such that for each fixed value of $x = tN^\phi$, where $t = (T - T_\theta)/T_\theta$,

$$Q(T, N) \sim N^{q_\theta} G(tN^\phi) \text{ as } N \rightarrow \infty. \quad (4)$$

(Note that Ref. [11] contains numerous typesetting errors in some formulas, such as Eq. (26), that makes readability less than optimal—see Ch. 2 in Ref. [12] for a nice summary.) Moreover, and importantly, it is assumed [17] that this asymptotic form provides all the dominant asymptotics for small t so that

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$$G(x) \sim \begin{cases} b_+ x^{(q_+ - q_\theta)/\phi}, & x \rightarrow \infty \\ b_- (-x)^{(q_- - q_\theta)/\phi}, & x \rightarrow -\infty. \end{cases} \quad (5)$$

This means that the high- and low-temperature forms, Eqs. (1) and (2), respectively, are recovered in the appropriate limits. Consequently, it further implies that

$$a_+(T) \sim b_+ t^{(q_+ - q_\theta)/\phi} \text{ as } t \rightarrow 0^+ \quad (6)$$

and

$$a_-(T) \sim b_+ (-t)^{(q_- - q_\theta)/\phi} \text{ as } t \rightarrow 0^-. \quad (7)$$

Since these exponents often have separate definitions, a crossover theory provides relationships between exponents defined by asymptotics in N at $T = T_\theta$ and asymptotics in t on approaching T_θ . We note that suitable adjustments can sometimes be made to this scenario if some or all of the asymptotic behaviors are not algebraic, for example, in the scaling of the partition function where exponential as well as algebraic factors arise [11].

Armed with the general principle of crossover scaling described above, it is a simple matter to deduce answers to the questions posed in GH. First, the density $\hat{\rho}$ inside the collapsed polymer is considered on approaching T_θ from below. Since the density is defined as

$$\hat{\rho}(T) = \lim_{N \rightarrow \infty} \rho(T, N) = \lim_{N \rightarrow \infty} \frac{N}{R_g(T, N)^d}, \quad (8)$$

where $R_g(T, N)$ is the radius of gyration [which is a quantity obeying the rules above for a general quantity $Q(T, N)$], we can then relate how $\hat{\rho}(T)$ behaves on approaching T_θ . Because the polymer is expanded at high temperatures, $\hat{\rho}(T)$ is zero for $T \geq T_\theta$. For $T < T_\theta$, $R_g(T, N) \sim r_-(T) N^{1/d}$ so that $\rho(T, N) \sim r_-(T)^{-d}$. In fact, $\hat{\rho}(T)$ acts like an order parameter for the transition just as the density is an order parameter in a liquid-gas transition. Let us define β as

$$\hat{\rho}(T) \sim (-t)^\beta \text{ as } t \rightarrow 0^- \quad (9)$$

and ν_θ via $R_g(T_\theta, N) \sim r_\theta N^{\nu_\theta}$. Hence, using the crossover theory above, we have from the analogous formula to Eq. (7)

$$r_- \sim b_- (-t)^{(1/d - \nu_\theta)/\phi} \text{ as } t \rightarrow 0^- \quad (10)$$

and therefore

$$\beta = \frac{(d\nu_\theta - 1)}{\phi}. \quad (11)$$

In two dimensions Eq. (11) implies that $\beta = 1/3$, since $\nu_\theta = 4/7$ and $\phi = 3/7$ are expected [18]. This answers the question raised in Sec. II of GH. It also is well supported by the numerical evidence provided in HG, where it is estimated that $\beta_{2d} = 0.32$.

Also of interest in GH and HG is the scaling of the (reduced) surface free energy $s(T)$ in the collapsed phase. [Again $s(T) = 0$ for $T \geq T_\theta$.] $s(T)$ can be defined (up to a

factor dependent on the average shape of the surface) via the scaling of the polymer partition function in low temperatures [13,14],

$$Z(T, N) \sim e^{f(T)N + s(T)N^{(d-1)/d} + A_-(T)} N^{\gamma_- - 1}, \quad (12)$$

where $f(T)$ is the bulk (reduced) free energy per monomer, A_- is a nonconstant function of T , and γ_- may also be nonconstant. We shall first consider the simpler case, where γ_- is assumed constant. Let us define χ via

$$s(T) \sim c_- (-t)^\chi \text{ as } t \rightarrow 0^-. \quad (13)$$

Matching the crossover scaling form for the partition function,

$$Z(T, N) \sim e^{f(T_\theta)N} N^{\gamma_\theta - 1} H(tN^\phi), \quad (14)$$

with Eq. (12) implies that

$$H(x) \sim (-x)^{-(\gamma_\theta - \gamma_-)/\phi} e^{c_1(-x)^{1/\phi} + c_2(-x)^{(d-1)/d\phi}} \quad (15)$$

as $x \rightarrow -\infty$ with c_1 and c_2 being constants. This immediately gives

$$\chi = \frac{(d-1)}{d\phi}. \quad (16)$$

So for two dimensions $\chi = 7/6$ holds. At this point in the discussion it is important to note that χ will be difficult to estimate as it requires an accurate estimate of $s(T)$, which is part of a subdominant factor in the scaling of the partition function (or free energy), just in the region of temperature affected by strong crossover effects from the change in the γ exponent from γ_θ to γ_- .

Let us now return to the case where γ_- is considered to be a nonconstant function of temperature $\gamma_-(T)$ for $T \in [0, T_\theta]$. We shall assume that $\gamma_-(T)$ is a slowly varying function continuous on $(0, T_\theta)$. Let $\lim_{T \nearrow T_\theta^-} \gamma_-(T) = \hat{\gamma}_-$.

One possible scenario is to simply replace γ_- with $\hat{\gamma}_-$ in Eq. (15) to allow the crossover form (14) to match as $T \nearrow T_\theta^-$ the low-temperature form (12). One should note that the matching is always an approximate one valid in an asymptotic sense (see Ref. [17]) as $T \nearrow T_\theta^-$. For example, even in the simple case of the matching of algebraic singularities described by Eq. (5), the fixed temperature asymptotics, Eqs. (1) and (2), are only recovered for temperatures asymptotically close to T_θ , since the amplitudes are given only asymptotically. Here we have a subdominant confluent factor whose exponent would only be asymptotically matched. On the other hand it may also be the case that varying $\gamma_-(T)$ at low temperatures is also accompanied by a subtle breaking of classic scaling assumptions around T_θ .

In any case we remark that result (16) can be found from a scaling ansatz for a suitably defined finite sized surface free energy $s(T, N)$. Here the behavior of γ_- is unimportant. Assuming $s(T, N) \sim N^{-(d-1)/d} K(tN^\phi)$ for tN^ϕ fixed and then matching the fixed $T < T_\theta$ behavior of $s(T, N)$, namely,

that $\lim_{N \rightarrow \infty} s(T, N) = s(T) \neq 0$, implies $K(x) \sim (-x)^{(d-1)/d\phi}$ as $x \rightarrow -\infty$ from which the result again follows.

We have shown that questions such as those raised in recent stimulating work by Grassberger and Hsu [1,2] on the scaling of collapsing and collapsed polymers in low dimensions can be answered by the application of crossover scaling theory. Exponents defined by the singularity in temperature at the θ point can be related to those defined by fixed temperature scaling in the length and to the crossover exponent

ϕ . In particular, we conjecture a value of 1/3 for the temperature singularity of the globular density at the θ point in two dimensions. We also explain where the value of 7/6 in two dimensions arises for the temperature singularity of the surface free energy at the θ point.

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