Anomalous tricritical behaviour in the coil-globule transition of a single polymer chain

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We investigate a model of self-avoiding walk exhibiting a first-order coil-globule transition. This first-order nature, unravelled through the coexistence of distinct coil and globule populations, has observable consequences on the scaling properties. A thorough analysis of the size dependence of the mean radius of gyration evidences a breakdown of the plain tricritical scaling behaviour. In some regimes, anomalous exponents are observed in the transition region and logarithmic corrections arise along the coexistence curve.

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Experimental observations [1,2] as well as theoretical studies for a specific model [3,4] suggest that the coil-globule transition of an isolated self-avoiding walk of finite size N might exhibit first-order features. A strong evidence is the coexistence in some range of temperature of distinct coil and globule populations. Its theoretical signature is a bimodal shape of the order parameter distribution $P_N^{(3)}(t)$, where $t$ is some conformational parameter of the single chain, such that the transition is achieved through an exchange of weight between the two peaks as temperature varies. We here investigate the observable consequences of this first-order feature on the scaling behaviour of the chain in the transition region. Although one recovers a second-order transition in the infinite-size limit, one may wonder whether the standard tricritical picture of the $\Theta$-point [3,4] still applies. In previous studies [3,4], scaling arguments supplemented with Monte Carlo simulations of a self-avoiding chain on a cubic lattice provided an exact analytical expression for the entropic contribution $P_N^{(3)}(t)$ to the distribution $P_N^{(3)}(t)$ of the order parameter $t$, defined as [5]:

$$t = \rho^{1/(\nu d - 1)} = \left(\frac{N}{\rho^d}\right)^{5/4}$$  \hspace{1cm} (1)

where $\rho$ is the radius of gyration of the conformation and $\rho = N/\rho^d$ its mean density (here $d = 3$ and $\nu = 3/5$ is the Flory exponent). We then modelled the energy of the infinite-size limit, one may wonder whether the standard tricritical picture of the $\Theta$-point [3,4] still applies.

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$$\hat{t} = tN^{1/n} \text{ with } n \approx 2$$  \hspace{1cm} (2)

$$\hat{\tau} = \tau N^{\phi} \text{ with } \phi = 1 - \frac{1}{n} \text{ and } \tau = 1 - \frac{\theta}{T}$$  \hspace{1cm} (3)

where $\theta$ is a rough estimate of the transition temperature. We obtained the following expression for the equilibrium distribution:

$$\hat{P}_N(\hat{\tau}, \hat{t}) = \frac{h(\hat{\tau}, \hat{t}) e^{-A N^{-q(1-1/n)} \hat{t}^{-q}}}{I_c(N, \hat{\tau})}$$  \hspace{1cm} (4)

where

$$h(\hat{\tau}, \hat{t}) = \hat{c} e^{-\hat{A} \hat{t}^{-\hat{B} \hat{t}^n}}$$  \hspace{1cm} (5)

is the scale-invariant contribution. The factor $I_c(N, \hat{\tau})$ ensures that $\int_0^\infty \hat{P}_N(\hat{\tau}, \hat{t})d\hat{t} = 1$. Let us emphasize the key role of the factor $\hat{c}$: for $c < -1$, this factor, hence the function $h(\hat{\tau}, \hat{t})$, are not integrable in $\hat{t} = 0$. It forbids to take the infinite-size limit in $\hat{P}_N(\hat{\tau}, \hat{t})$ and to use the infinite-size system as a reference system. This factor $\hat{c}$ outweights the coil region and it will induce an observable breakdown of the scale invariance. More generally, we introduce for any real $z$:

$$I_z(N, \hat{\tau}) = \int_0^\infty \hat{t}^z e^{-A \hat{t}^{-B \hat{t}^n}} e^{-A N^{-q(1-1/n)} \hat{t}^{-q}} d\hat{t}$$  \hspace{1cm} (6)

An arbitrary moment simply writes:

$$< \hat{t}^\alpha > = \frac{I_{\alpha + c}(N, \hat{\tau})}{I_c(N, \hat{\tau})}$$  \hspace{1cm} (7)

Due to the factor $\hat{c}$, the scaling behaviour of $I_z(N, \hat{\tau})$ strongly depends on the sign of $z + 1$. For $z + 1 > 0$, it writes:

$$I_z \propto \begin{cases} \frac{1}{\tau^{z+1}} & \text{for } \hat{\tau} \gg 1 \\ \left(\frac{-A \hat{c}}{nB}\right)^{-q(1-1/n)} e^{(n-1)B(\frac{-A \hat{c}}{nB})^{n+1}} & \text{for } \hat{\tau} < 0, \ |\hat{\tau}| \gg 1 \end{cases}$$  \hspace{1cm} (8)

In the case where $z + 1 > 0$, $I_z(N, \hat{\tau})$ is thus asymptotically scale-invariant, depending only on the rescaled variable $\hat{\tau} = N^\phi \tau$ but no more on $N$.

For $z + 1 < 0$, two regimes occur on each side of a borderline $\hat{\tau}_\text{coex}(N, z)$, as shown on Figure 1:

$$I_z \propto \begin{cases} N^{-(z+1)(1-1/n)} & \text{above} \\ \left(\frac{-A \hat{c}}{nB}\right)^{-q(1-1/n)} e^{(n-1)B(\frac{-A \hat{c}}{nB})^{n+1}} & \text{below} \end{cases}$$  \hspace{1cm} (9)

Here arises the above-mentionned scale-invariance breakdown. It originates in the bimodal shape of $\hat{t}^\alpha \hat{P}_N(\hat{\tau}, \hat{t})$:
when $\tilde{\tau}$ decreases, a “coil” peak is quite abruptly replaced by a “globule” peak after a coexistence regime precisely located around the curve $\tilde{\tau}_\text{coex}(N, z)$. Writing that the two peaks of $\tilde{t}^{-c}P_N(\tilde{\tau}, \tilde{t})$ coexist with equal weights (which requires $z + 1 < 0$) yields the following implicit equation for the borderline $\tilde{\tau}_\text{coex}(N, z)$:

$$-\phi(1 + z)\ln N = (n - 1)B \left( \frac{-A\tilde{\tau}}{nB} \right)^{\frac{z}{n-1}} + \ln C_z + z\ln |\tilde{\tau}| - \frac{\phi}{n-1}$$

(10)

where $C_z$ is some numerical constant. $\tilde{\tau}_\text{coex}(N, z)$ could have been obtained straightforwardly by writing the balance between the two expressions of $\mathcal{I}_z$ given in Eq.(3).

For large $N$, $\tilde{\tau}_\text{coex}(N, z) \propto (\ln N)^\phi$ for any value $z < -1$. The borderline $\tilde{\tau}_\text{coex}(N, z)$ thus separates the domain in $(\tilde{\tau}, \ln N)$-space where the globule peak is overwhelming, leading to a scale-invariant expression for $\mathcal{I}_z$, and the domain where the coil peak is overwhelming. In the latter domain, the behaviour of $\mathcal{I}_z$ is ruled by the coil peak, being controlled only by the size $N$ (independent of $\tilde{\tau}$ at fixed $N$). Note that we are here reasoning on the peaks of $\tilde{t}^{-c}P_N(\tilde{\tau}, \tilde{t})$ so that the two peaks cannot be exactly identified with the coil and the globule phases, unless $z = c$.

In the special instance where $z = c$, $\tilde{\tau}_\text{coex}(N, c)$ is then the “true” coexistence line where the coil and globule populations are equally weighted; it writes more explicitly (denoting $\theta = \theta(\infty)$):

$$\theta(N) - \theta = \frac{\tilde{\tau}_\text{coex}(N, c)}{N^\phi} \propto \left( \frac{\ln N}{N} \right)^\phi$$

(11)

Let us note that the value $n = 2$ is consistent with the predicted value $\phi = 1/2$ for the crossover exponent [2], since here $\phi = 1 - 1/n$.

Observable quantities are related to the moments of the distribution $P_N(\tilde{\tau}, \tilde{t})$. Recalling that $r = N^{1/d}t^{1/d-\nu} = N^{\nu}t^{1/d-\nu}$, where:

$$\nu_0 = \frac{1}{d} + \frac{1}{n} (\nu - \frac{1}{d})$$

(12)

we introduce a generalised mean radius of gyration as:

$$R_\alpha = N^{1/d} < t^\alpha > -\frac{\nu-1/d}{d} = N^{\nu_0} < \tilde{t}^\alpha > -\frac{\nu-1/d}{d}$$

(13)

for any nonzero real $\alpha$. Scaling behaviour of the moment $< \tilde{t}^\alpha >$ follows from the behaviour of $\mathcal{I}_c$ and $\mathcal{I}_{\alpha+c}$ (see Eq.(5)). Of special interest are the values $\alpha = 1$, as $R_1$ is related to the mean value $< t >$, and $\alpha = -2(\nu - 1/d)$, leading to the standard mean radius of gyration $R_G = < r^2 >^{1/2}$, that can be measured through scattering experiments. For fixed $\tilde{\tau} < 0$, one recovers the foreseeable globule scaling law $R_\alpha \propto N^{1/d}$ (here $d = 3$) whereas for fixed $\tilde{\tau} > 0$, one recovers the coil scaling law $R_\alpha \propto N^\nu$, whatever $\alpha$ is. In between, in the transition region $|\tilde{\tau}| \to 0$, $\tilde{\tau}$ finite, various scaling regimes are observed, depending on the sign of $1 + c$ and $1 + c + \alpha$. The different cases are sketched on Figure 2.

If $c > -1$ and $\alpha + c > -1$ (case 1), the ratio $\mathcal{I}_{\alpha+c}/\mathcal{I}_c$ is scale-invariant; it follows that $R_\alpha$ exhibits the standard tricritical behaviour:

$$R_\alpha \propto N^\nu f(\tilde{\tau}) = N^\nu f(N^\theta \tau)$$

with

$$f(\tilde{\tau}) \propto \begin{cases} |\tilde{\tau}|^{-\left(\frac{\nu}{n-1}\right)} & \text{for } \tilde{\tau} < 0, |\tilde{\tau}| \gg 1 \\ \tilde{\tau}^{-\left(\nu-1/d\right)} & \text{for } \tilde{\tau} > 0, |\tilde{\tau}| \gg 1 \end{cases}$$

(15)

For negative and large $\tilde{\tau} = N^\theta \tau$, one recovers the usual scaling behaviour $R_\alpha \propto N^{\nu(1)}$; this crossover reflects in the hyperscaling relation:

$$\nu_0 - \phi \left( \nu - \frac{1}{d} \right) \left( \frac{1}{n-1} \right) = \frac{1}{d}$$

(16)

whereas for positive and large $\tilde{\tau} = N^\theta \tau$, one recovers the usual scaling behaviour $R_\alpha \propto N^\nu$; this crossover reflects in the hyperscaling relation:

$$\nu_0 + \phi \left( \nu - \frac{1}{d} \right) = \nu$$

(17)

As soon as $c \leq -1$ or $\alpha + c \leq -1$ (cases 2 to 5), scale-invariance breakdown and anomalous behaviour are observed. The scaling law for $R_\alpha$ still writes:

$$R_\alpha \propto N^{\nu(1)} |\tilde{\tau}|^{-\left(\frac{\nu}{n-1}\right)(\nu-\frac{\nu}{2})}$$

(19)

But the exponent $\nu_{eff}$ and the scaling function $f$ change when passing across the curves $\tilde{\tau}_\text{coex}(N, c)$ and $\tilde{\tau}_\text{coex}(N, \alpha+c)$. It is clear that $\phi = 1 - 1/n$ is the crossover exponent. In any cases (2 to 5), both $\mathcal{I}_{\alpha+c}$ and $\mathcal{I}_c$ are scale-invariant in the leftmost region. For $\tilde{\tau} < 0$ with $|\tilde{\tau}|$ enough large, any observable $R_\alpha$ thus exhibits the scaling behaviour yet encountered in case 1:

$$R_\alpha \propto N^\nu |\tilde{\tau}|^{-\left(\frac{\nu}{n-1}\right)(\nu-\frac{\nu}{2})}$$

(19)

For $|\tilde{\tau}| \gg 1$, one recovers the usual scaling behaviour $R_\alpha \propto N^{1/d}$, for any $\alpha$, according to the hyperscaling relation given in Eq.(14).

In cases 2 to 5, the key point is the emergence of an intermediate region where either $\mathcal{I}_{\alpha+c}$, either $\mathcal{I}_c$, or both behave as $\tilde{\tau}$-independent powers of $N$. This modifies the exponent $\nu_0$ into an anomalous exponent:

$$\nu_0'(\alpha) = \nu_0 - \phi \left( \frac{1 + c}{\alpha} \right) \left( \nu - \frac{1}{d} \right)$$

(20)

observed for $\alpha > 0$ or:

$$\nu_0''(\alpha) = \nu_0 + \phi \left( \frac{1 + c}{\alpha} \right) \left( \nu - \frac{1}{d} \right)$$

(21)
observed for $\alpha < 0$. The axis $\hat{\tau} = 0$ plays no particular role. In cases 2 and 3, only one curve exists, respectively $\hat{\tau}_{\text{coex}}(N, \alpha + c)$ and $\hat{\tau}_{\text{coex}}(N, c)$. On its right side (i.e. above it), $R_\alpha$ behaves respectively as $N^{\nu_0} f_2(\hat{\tau})$ and $N^{\nu_0'} f_3(\hat{\tau})$ where $f_2$ and $f_3$ are complicated (but independent of $N$) functions of $\hat{\tau}$. Both reduce to a power law for $\hat{\tau} \gg 1$:

$$f_2(\hat{\tau}) \propto \hat{\tau}^{-\left(\frac{\alpha + 1}{\alpha}\right)(\nu - \frac{1}{d})}$$
$$f_3(\hat{\tau}) \propto \hat{\tau}^{-\left(\frac{\alpha + c + 1}{\alpha}\right)(\nu - \frac{1}{d})}$$

(22)

Using definitions (20) and (21), we obtain hyperscaling relations:

$$\nu_0^' + \phi \left(\frac{\alpha + c + 1}{\alpha}\right) \left(\nu - \frac{1}{d}\right) = \nu$$

(23)

and

$$\nu_0^' - \phi \left(\frac{c + 1}{\alpha}\right) \left(\nu - \frac{1}{d}\right) = \nu$$

(24)

ensuring that the expected scaling behaviour $R_\alpha \propto N^\nu$ is recovered as soon as $\hat{\tau} \gg 1$. Note that the mean order parameter $<t>$ and the associated mean radius of gyration $R_1$ belong to case 3 ($c = -1.13$ and $\alpha = 1$).

In the last cases (4 and 5), the anomalous exponent is observed in the intermediate but unbounded region located between $\hat{\tau}_{\text{coex}}(N, c)$ and $\hat{\tau}_{\text{coex}}(N, \alpha + c)$. It is still equal to $\nu_0^'(\alpha)$ for $\alpha > 0$ and $\nu_0^''(\alpha)$ for $\alpha < 0$. In these cases, the exponent $\nu$ is observed in the rightmost region, even if $\hat{\tau}$ is not large with respect to 1 (even negative). Note that the mean radius of gyration $\sqrt{\nu}^2 > 1/2$ belongs to case 4 ($c = -1.13$ and $\alpha + c = -1.66$).

The remarkable features unravelled here are:

(i) the exchange of weight between the coil phase and the globule phase is far sharper with respect to the variation of $\hat{\tau}$ when it occurs through the coexistence of two peaks than when it occurs through the shift of a simple peak. Accordingly, a sharp crossover is observed in the behaviour of $I_\alpha$ if $z + 1 < 0$, located in a narrow stripe of width $(\log N)^{-\phi}$ around $\hat{\tau}_{\text{coex}}(N, z)$, whereas a slow change with a scale-invariant behaviour of $I_\alpha$ is observed for $z + 1 > 0$.

(ii) due to the $N$-dependence of the curves $\hat{\tau}_{\text{coex}}(N, z)$ for $z + 1 < 0$, a size-controlled crossover occurs at the passage across the curves $\hat{\tau}_{\text{coex}}(N, c)$ (if $c < -1$) or $\hat{\tau}_{\text{coex}}(N, \alpha + c)$ (if $\alpha + c < -1$).

(iii) either case, either $\alpha + c$ or both are lower than $-1$ (cases 2 to 5 of Figure 2), an intermediate region arises where an anomalous exponent (neither $\nu$ nor $\nu_0^'$) is observed. Usual tricritical scaling is observed only for $c > -1$ and $\alpha + c > -1$ (case 1 of Figure 2).

(iv) for $c < -1$ (cases 3 to 5 of Figure 2), on the coexistence line $\hat{\tau}_{\text{coex}}(N, c)$, the scaling behaviour of $R_\alpha$ exhibits multiplicative logarithmic corrections with the same exponent whatever $\alpha$ is:

$$R_\alpha = N^{\nu_0}(\ln N)^{-\frac{1}{d}(\nu - 1/d)} = N^{\nu_0}(\ln N)^{-\frac{1}{d}\hat{\tau}}$$

(25)

What we here suggest is that the scaling behaviour around the $\Theta$-point might be more complex than the standard tricritical behaviour \[3\] \[1\]. The peculiarity of the scaling behaviour associated with the first-order features of the transition is the occurrence of two “theta regimes”. A first one is observed when the globule peak is overwhelming; it thus involves the exponent $\nu_0$ arising from the scale invariance of the globule phase and the scaling function is a power law. A second, anomalous one involves an observable-dependent exponent $\nu_0^'(\alpha)$ (if $c < -1$ and $\alpha > 0$) or $\nu_0^''(\alpha)$ (if $\alpha + c < -1$ and $\alpha < 0$) where $\alpha$ refers to the observable $R_\alpha$; this anomalous exponent arises from a non trivial balance between the scale invariant globule phase and the size-controlled coil phase, which is required to match their incompatible scaling behaviours. Only the detailed analysis of equilibrium distributions like $P_N^\prime(\tau)$ gives reliable predictions about the actual coil-globule transition experienced by a chain of finite size.

A related result is the irrelevance of standard finite-size scaling approaches to describe the size dependence of the thermal coil-globule transition. Indeed, the standard finite-size analysis used for first-order transitions \[3\] here failed as the two states merge in the infinite-size limit. On the other hand, an analysis based on the knowledge of the infinite-size second-order transition \[3\] cannot account for the first-order features here observed in finite size. In a word, standard finite-size scaling approaches are designed to predict the rounding of the transition features in finite size but cannot introduce back the change of nature of the transition observed here. A novel finite-size scaling analysis should thus be designed to interpret experimental or numerical data \[10\].

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Captions

Figure 1: Scaling behaviour of $I_z$ for $z + 1 < 0$ (here $z = -1.66$, corresponding to the integral $I_{\alpha+c}$ involved in the mean radius of gyration $\langle r^2 \rangle^{1/2}$). The two scaling regimes are separated by the curve $\hat{\tau}_{\text{coex}}(N, z)$, depending on $z$ but of similar shape for any value $z < -1$. The curve is restricted to the domain $\hat{\tau} \leq \hat{\tau}_g \approx -3.2$ (independent of $N$) where a well-identified globule state (a globule peak) exists. For $c < -1$, $\hat{\tau}_{\text{coex}}(N, z = c)$ is the coexistence line of the then first-order coil-globule transition.

Figure 2: Critical exponents of $R_{\alpha}(N, \hat{\tau})$ for the different scaling regimes determined by the signs of $1 + c$ and $1 + \alpha + c$. The bold line (cases 3, 4 and 5) is the coexistence curve $\hat{\tau}_{\text{coex}}(N, c)$ (defined for $c + 1 < 0$, here $c = -1.13$); the thin line (cases 2, 4 and 5) is the curve $\hat{\tau}_{\text{coex}}(N, \alpha + c)$ (defined for $1 + \alpha + c < 0$, here $\alpha + c = -1.66$ which corresponds to the mean radius of gyration $\langle r^2 \rangle^{1/2}$).
\[ J_z \sim N^{-(1+z)(1-\frac{1}{n})} \]

\[ J_z \sim \left(\frac{-A\hat{\tau}}{nB}\right)^{\frac{n-1}{2}} \exp^{(n-1)B\left(\frac{-A\hat{\tau}}{nB}\right)^{\frac{n-1}{2}}} \]
Case 1: $c < -1$ , $\alpha + c < -1$

Case 2: $\alpha + c < -1 < c$

Case 3: $c < -1 < \alpha + c$

Case 4: $\alpha + c < c < -1$

Case 5: $c < \alpha + c < -1$