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# Polymer collapse in supercritical solvents

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We show analytically that in dilute solutions of high molecular weight polymers, a collapse transition of the chain can be induced by proximity to the critical point of the solvent. The transition is driven by the fluctuations in the medium, which lead to an effective attractive interaction of long range between different parts of the polymer. At the critical point itself, however, the chain adopts the same average conformations that characterize its size in the off-critical limit. In other words, on approach to the critical point, the polymer is found first to contract and collapse, and then subsequently to return to its original dimensions. This behavior has recently been observed in simulations of polymer-solvent mixtures near the lower critical solution temperature of the system, and it is also known to be characteristic of solutions of polymers in bicomponent solvent mixtures near the critical consolute point of the two solvents. © 1999 American Institute of Physics. [S0021-9606(99)50431-5]

## I. INTRODUCTION

The possibility that large scale solvent fluctuations in polymer solutions might be instrumental in producing dramatic changes to chain conformational behavior seems to have first been seriously investigated by de Gennes,<sup>1</sup> who showed, with Brochard,<sup>2</sup> that polymers in the vicinity of the critical consolute point of a bicomponent solvent mixture would first collapse, and then, at the critical point itself, re-expand. Vilgis, Sans, and Jannink<sup>3</sup> (VSJ) later reached much the same conclusions using a somewhat more elaborate field theoretic reformulation of Brochard and de Gennes's scaling arguments. Numerical simulations have tended to confirm these predicted effects,<sup>4,5</sup> but only recently has experimental evidence — gathered from measurements of light scattering in solutions of polyacrylic acid in water and 2,6-lutidine— shown that the effects appear to be real.<sup>6</sup> The origin of fluctuation-induced conformational transitions is generally believed to lie in the preferential adsorption of one of the solvent components onto the polymer,<sup>1,2,7</sup> and the screening out, as a result, of excluded volume interactions between different parts of the chain, with the degree of “wetting” between solvent and polymer being determined by proximity to the critical point of the solvent mixture.

Recent simulations of isolated chains in a single solvent near the lower critical solution temperature (LCST) of the solution, reveal strikingly similar effects, including partial chain collapse and re-expansion.<sup>8,9</sup> LCST behavior is well known to occur in solutions of polymers in supercritical fluids (SCFs)<sup>10</sup> — indeed the LCST is often very near the gas-liquid critical point of the pure solvent<sup>9</sup> — so a general theory of polymer behavior in SCFs, apart from its own intrinsic importance,<sup>11,12</sup> could be expected to offer insights into these numerical results. No such theory is yet available, but given the dominant role of fluctuations in critical phenomena, the methods of field theory — as developed in the analysis of VSJ, for example — would seem to provide the natural starting point for its construction. However, the VSJ

treatment of polymers in near critical solvent mixtures does not itself allow for a consideration of the problem of a polymer in a single solvent. The parameters that describe the interaction of the polymer with the two solvents are required to be distinct, and the limit in which they are made identical leads to the complete decoupling of polymer and solvent. Moreover, although the formalism is couched in the language of field theory, it relies ultimately on a simplified version of Flory theory to derive relations between chain dimensions and critical fluctuations. A separate and more rigorous description of the polymer-SCF situation is therefore desirable, and the present paper is an attempt to provide such a description.

The following section outlines the derivation of an expression for the size of a chain in a polymer-solvent mixture. The derivation proceeds essentially by averaging the Hamiltonian of the two-component system over the configurational degrees of freedom of the solvent alone. An additional attractive interaction is generated thereby that can be expressed in terms of the structure factor of the pure solvent. Within the present level of approximation, the structure factor contains all the details that describe the effects of critical fluctuations on the equilibrium properties of the polymer. Section III describes the actual evaluation of the mean square end-to-end distance  $\langle R^2 \rangle$  of the chain using the Edwards–Singh method.  $\langle R^2 \rangle$  is found to depend on the ratio  $\alpha$  of the size of the chain to the correlation length of the solvent density fluctuations. Section IV derives the scaling relations between  $R$  and chain length  $N$  for various limiting values of  $\alpha$ , and Sec. V briefly presents some general conclusions.

## II. THEORY

The starting point of our calculations is the following expression for the mean square end-to-end distance  $\langle R^2 \rangle$  of a single chain in a fluid:

$$\langle R^2 \rangle = \lim_{\lambda \rightarrow 0} \frac{\partial}{\partial \lambda} \ln Z(\lambda), \tag{1}$$

where  $Z(\lambda)$ , defined below, is the configurational partition function of the polymer-solvent mixture evaluated at some value of a parameter  $\lambda$ :

$$Z(\lambda) = \int \mathcal{D}[1] \int \mathcal{D}[2] \exp \left[ -H + \lambda \int_0^N d\tau \dot{\mathbf{r}}(\tau) \cdot \int_0^N d\tau \dot{\mathbf{r}}(\tau) \right]. \tag{2}$$

Here, the symbols  $\mathcal{D}[1]$  and  $\mathcal{D}[2]$  stand for the measures on the space of conformations of polymer (component 1) and solvent (component 2). The conformations of the polymer are described by the continuous curve  $\mathbf{r}(\tau)$ , which defines the spatial location, in Cartesian coordinates, of the monomer at the point  $\tau$ .<sup>13</sup>  $N$  is the total length of the polymer along its contour, while  $\int_0^N d\tau \dot{\mathbf{r}}(\tau) (= \mathbf{r}(N) - \mathbf{r}(0) \equiv \mathbf{R})$  is the end-to-end distance of the chain, the origin of coordinates being taken to coincide with the position of the first monomer. The solvent is viewed as a collection of  $n$  point particles whose positions in space are described by the vectors  $\mathbf{q}_i$ ,  $i = 1, \dots, n$ .  $H$  is the Hamiltonian of the system in units of the thermal energy  $k_B T$ , and is given by

$$H = H_1 + H_2 + H_{12}. \tag{3}$$

The polymer Hamiltonian  $H_1$  is assumed to be of the form<sup>13</sup>

$$H_1 = \frac{3}{2l} \int_0^N d\tau \left| \frac{\partial \mathbf{r}(\tau)}{\partial \tau} \right|^2 + \frac{1}{2} g_0 \int_0^N d\tau \int_0^N d\tau' \delta[\mathbf{r}(\tau) - \mathbf{r}(\tau')], \tag{4}$$

where  $l$  is the Kuhn length between effective chain segments, and  $g_0$  is a dimensional parameter that is a measure of the strength of *repulsive* excluded volume interactions. The solvent Hamiltonian  $H_2$  is written as

$$H_2 = \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n V^{(22)}(\mathbf{q}_i - \mathbf{q}_j), \tag{5}$$

where  $V^{(22)}$  is a pair potential whose exact form will not need to be specified. The mixed term  $H_{12}$ , representing interactions between polymer and solvent, is expressed as

$$H_{12} = \sum_{i=1}^n \int_0^N d\tau V^{(12)}[\mathbf{r}(\tau) - \mathbf{q}_i] \tag{6}$$

which can be written in the equivalent form

$$H_{12} = \frac{1}{(2\pi)^3} \int d\mathbf{k} \hat{V}^{(12)}(\mathbf{k}) \hat{\rho}_1(-\mathbf{k}) \hat{\rho}_2(\mathbf{k}), \tag{7}$$

where  $\hat{\rho}_1$  and  $\hat{\rho}_2$  are the Fourier transforms of the local monomer and solvent density, respectively, which are defined by

$$\rho_1(\mathbf{r}) = \int_0^N d\tau \delta[\mathbf{r} - \mathbf{r}(\tau)], \tag{8}$$

$$\rho_2(\mathbf{r}) = \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{q}_i). \tag{9}$$

$Z(\lambda)$  may now be re-expressed as

$$Z(\lambda) = Z_2 \int \mathcal{D}[1] \exp \left[ -H_1 + \lambda \int_0^N d\tau \frac{\partial \mathbf{r}(\tau)}{\partial \tau} \cdot \int_0^N d\tau \frac{\partial \mathbf{r}(\tau)}{\partial \tau} \right] \langle e^{-H_{12}} \rangle \tag{10}$$

by introducing into Eq. (2) the configurational partition function of the solvent,  $Z_2 = \int \mathcal{D}[2] \exp(-H_2)$ , and defining a solvent average  $\langle \dots \rangle$  as

$$\langle \dots \rangle = \frac{1}{Z_2} \int \mathcal{D}[2] (\dots) e^{-H_2}. \tag{11}$$

Employing a cumulant expansion for the average in Eq. (10), and truncating the expansion at second order, we can readily show that

$$\langle R^2 \rangle = \lim_{\lambda \rightarrow 0} \frac{\partial}{\partial \lambda} \ln e^{-\bar{\rho}_1 \bar{\rho}_2 \hat{V}^{(12)}(0)} \int \mathcal{D}[1] \exp \left[ -H_1 + \lambda \int_0^N d\tau \dot{\mathbf{r}}(\tau) \cdot \int_0^N d\tau \dot{\mathbf{r}}(\tau) + \frac{1}{2(2\pi)^3} \int d\mathbf{k} |\hat{V}^{(12)}(\mathbf{k})|^2 |\hat{\rho}_1(\mathbf{k})|^2 \hat{S}_{22}(\mathbf{k}) \right], \tag{12}$$

where  $\bar{\rho}_1$  and  $\bar{\rho}_2$  are the mean monomer and solvent densities, respectively, and  $\hat{S}_{22}(\mathbf{k})$  is the equilibrium structure factor of the pure solvent. In truncating the cumulant expansion at second order, we are assuming, implicitly, that the coupling between monomer and solvent is weak. A more thorough analysis incorporating cubic and quartic corrections<sup>14</sup> may be carried out, but for the present purposes, the present level of detail is expected to be adequate.

In the same vein, by virtue of the importance of long wavelength density fluctuations to the near-critical behavior of the solvent, it should be possible to write, as a further simplifying approximation:

$$\hat{V}^{(12)}(\mathbf{k}) = \hat{V}^{(12)}(\mathbf{0}). \tag{13}$$

We also approximate the solvent structure factor by its Ornstein-Zernicke form:

$$\hat{S}_{22}(\mathbf{k}) = \rho_2 k_B T \kappa_T \frac{\xi^{-2}}{k^2 + \xi^{-2}}, \tag{14}$$

which is expected to interpolate fairly accurately between the near and off-critical limits in the small  $k$  limit. In Eq. (14),  $\kappa_T$  is the isothermal compressibility of the solvent, and  $\xi$  is the correlation length of density fluctuations. Somewhat better analytic representations of the structure factor are known,<sup>15,16</sup> but their use here is unlikely to alter the final conclusions qualitatively or even to be fully justified given the other approximations that have been made.

The end-to-end distance is now given by

$$\langle R^2 \rangle = \frac{1}{Q} \int d\mathbf{R} \int_{\mathbf{r}(0)=0}^{\mathbf{r}(N)=\mathbf{R}} \mathcal{D}[\mathbf{r}(\tau)] R^2 \exp \left\{ -\frac{3}{2l} \int_0^N |\dot{\mathbf{r}}(\tau)|^2 - \frac{1}{2} g_0 \int_0^N d\tau \int_0^N d\tau' \delta[\mathbf{r}(\tau) - \mathbf{r}(\tau')] + H_I \right\} \quad (15)$$

$$\equiv \frac{1}{Q} \int d\mathbf{R} \int_{\mathbf{r}(0)=0}^{\mathbf{r}(N)=\mathbf{R}} \mathcal{D}[\mathbf{r}(\tau)] R^2 \exp(-H_0 - H_V + H_I), \quad (16)$$

where  $H_0$  is the chain connectivity term,  $H_V$  is the term describing excluded volume interactions, and  $H_I$  is an effective attractive interaction term defined by

$$H_I = \frac{1}{2(2\pi)^3} \mu_0 \int_0^N d\tau \int_0^N d\tau' \int d\mathbf{k} \frac{1}{k^2 + \xi^{-2}} \exp\{-i\mathbf{k} \cdot [\mathbf{r}(\tau) - \mathbf{r}(\tau')]\}, \quad (17)$$

where

$$\mu_0 = \hat{V}^{(12)}(0)^2 \rho_2 k_B T \kappa_T \xi^{-2}. \quad (18)$$

The quantity  $Q$  in the denominator of Eqs. (15) and (16) is identical to the numerator except that it has no factor of  $R^2$ .

### III. THE EDWARDS-SINGH METHOD

The evaluation of  $\langle R^2 \rangle$  in Eq. (16) is most conveniently carried out using the self-consistent perturbative scheme developed by Edwards and Singh.<sup>17</sup> The details of the method are fairly well known, so we shall discuss its application to the present problem only briefly. The basic idea behind the method is to introduce into the given Hamiltonian the following reference Hamiltonian  $H_R$  involving an unknown step length  $l_1$ :

$$H_R = \frac{3}{2l_1} \int_0^N d\tau |\dot{\mathbf{r}}(\tau)|^2, \quad (19)$$

such that

$$\langle R^2 \rangle = \frac{\int \mathcal{D}[\mathbf{r}(\tau)] R^2 \exp[-H_R - (H_0 - H_R) - H_V + H_I]}{\int \mathcal{D}[\mathbf{r}(\tau)] \exp[-H_R - (H_0 - H_R) - H_V + H_I]}. \quad (20)$$

The exponentials in the numerator and denominator are now linearized around the reference Hamiltonian, whereupon to first order in the expansion,  $\langle R^2 \rangle$  is found to be given by

$$\begin{aligned} \langle R^2 \rangle &= \langle R^2 \rangle_R - \langle R^2(H_0 - H_R) \rangle_R + \langle R^2 \rangle_R \langle H_0 - H_R \rangle_R \\ &\quad - \langle R^2 H_V \rangle_R + \langle R^2 \rangle_R \langle H_V \rangle_R + \langle R^2 H_I \rangle_R \\ &\quad - \langle R^2 \rangle_R \langle H_I \rangle_R, \end{aligned} \quad (21)$$

where the angular brackets denote an average with respect to the probability distribution of the reference Hamiltonian. The requirement that  $\langle R^2 \rangle = Nl_1$  identically demands that the terms beyond the first on the right hand side of Eq. (21) sum to zero, a condition that determines the value of the unknown step length  $l_1$  as a function of  $N$  and the other parameters that define the Hamiltonian. The averages appearing in Eq. (21) are easily calculated; they are

$$\langle R^2 \rangle_R = Nl_1, \quad (22)$$

$$\langle R^2(H_0 - H_R) \rangle_R - \langle R^2 \rangle_R \langle H_0 - H_R \rangle_R = Nl_1^2 \left( \frac{1}{l} - \frac{1}{l_1} \right), \quad (23)$$

$$\begin{aligned} \langle R^2 H_V \rangle_R - \langle R^2 \rangle_R \langle H_V \rangle_R \\ = -\frac{g_0 l_1^2}{9(2\pi)^2} \int_0^\infty dk \int_0^N d\tau \int_0^N d\tau' |\tau - \tau'|^2 \\ \times k^4 \exp(-k^2 l_1 |\tau - \tau'|/6), \end{aligned} \quad (24)$$

$$\begin{aligned} \langle R^2 H_I \rangle_R - \langle R^2 \rangle_R \langle H_I \rangle_R \\ = -\frac{\mu_0 l_1^2}{9(2\pi)^2} \int_0^\infty dk \int_0^N d\tau \int_0^N d\tau' |\tau - \tau'|^2 \\ \times \frac{k^4}{k^2 + \xi^{-2}} \exp(-k^2 l_1 |\tau - \tau'|/6). \end{aligned} \quad (25)$$

All the integrals in the above equations may be evaluated analytically. The condition  $\langle R^2 \rangle = Nl_1$  then leads to

$$\begin{aligned} Nl_1^2 \left( \frac{1}{l} - \frac{1}{l_1} \right) &= \frac{\sqrt{6} g_0 N^{3/2}}{\pi^{3/2} l_1^{1/2}} - \frac{216 \mu_0 \xi^5}{\pi l_1^2} \left\{ e^\alpha [1 - \Phi(\sqrt{\alpha})] \right. \\ &\quad \left. \times \left( 1 - \frac{2}{3} \alpha + \frac{1}{6} \alpha^2 \right) + 2 \sqrt{\frac{\alpha}{\pi}} - \frac{\alpha}{3} - 1 \right\}, \end{aligned} \quad (26)$$

where  $\alpha$  is the ratio  $Nl_1/6\xi^2 \equiv \langle R^2 \rangle/6\xi^2$ , and  $\Phi$  is the probability integral.<sup>18</sup>

### IV. RESULTS

Depending on the relative magnitudes of the terms on the right hand side of Eq. (26), several solutions for  $l_1$  are clearly possible, but three limiting situations are of greatest interest. These are defined by (i)  $\langle R^2 \rangle \gg 6\xi^2$ , which corresponds to the regime of weak critical fluctuations, and hence to temperatures far from the critical temperature  $T_c$ , (ii)  $\langle R^2 \rangle \ll 6\xi^2$ , which corresponds to the regime of strong critical fluctuations, and hence to temperatures close to  $T_c$ , and (iii)  $\langle R^2 \rangle = 6\xi^2$ , which corresponds to a regime intermediate between (i) and (ii).

Away from the critical point, i.e., in region (i), the asymptotic expansion of the probability integral<sup>18</sup> simplifies Eq. (26) to

$$Nl_1^2 \left( \frac{1}{l} - \frac{1}{l_1} \right) = \frac{\sqrt{6} g_0 N^{3/2}}{\pi^{3/2} l_1^{1/2}} - \frac{\sqrt{6} \mu_0 \xi^2 N^{3/2}}{\pi^{3/2} l_1^{1/2}}. \quad (27)$$

An analytic solution to this equation (a fifth-order polynomial in the variable  $\sqrt{l_1/l}$ ) is not yet known, but  $l_1$  can be determined approximately in the limit  $1/l \gg 1/l_1$  and  $g_0 N^{1/2}$  large. Here

$$l_1 = \left( \frac{\sqrt{6} g_0 l}{\pi^{3/2}} \right)^{2/5} N^{1/5}. \quad (28)$$

This result, when combined with the expression  $\langle R^2 \rangle = Nl_1$ , leads to the scaling relation

$$R \sim N^{3/5}. \quad (29)$$

Thus, away from the critical point, the chain is in the swollen state of fully developed excluded volume.

Near the critical point, i.e., in region (ii), the series expansion of the probability integral simplifies Eq. (26) to

$$Nl_1^2 \left( \frac{1}{l} - \frac{1}{l_1} \right) = \frac{\sqrt{6}g_0N^{3/2}}{\pi^{3/2}l_1^{1/2}} - \frac{\sqrt{2}\mu_0N^{5/2}l_1^{1/2}}{15\sqrt{3}\pi^{3/2}}. \quad (30)$$

Again, a sensible analytic solution to this equation can be determined only in the limit  $l/l_1 \gg 1/l_1$  and  $g_0N^{1/2}$  large, where, as before

$$l_1 = \left( \frac{\sqrt{6}g_0l}{\pi^{3/2}} \right)^{2/5} N^{1/5}, \quad (31)$$

which leads to the same scaling relation as Eq. (29), viz.,

$$R \sim N^{3/5}. \quad (32)$$

Thus, in the immediate neighborhood of the critical point, the dimensions of the chain are also those of the fully swollen state. [A formal solution to Eq. (30) can also be derived in the limit  $l/l_1 \gg 1/l_1$ , provided the amplitude of excluded volume interactions is small, and the second term on the right hand side of the equation is larger than the first, but the result,  $l_1 \sim N^3$ , violates the condition assumed in its derivation, so it cannot be considered an acceptable solution.]

In the intermediate regime defined by condition (iii), Eq. (26) immediately reduces to

$$Nl_1^2 \left( \frac{1}{l} - \frac{1}{l_1} \right) = \frac{\sqrt{6}g_0N^{3/2}}{\pi^{3/2}l_1^{1/2}} - \frac{36\mu_0\xi^5B}{\pi l_1^2} \quad (33)$$

$$\equiv T_1 - T_2, \quad (34)$$

where  $B = 3\pi e[1 - \Phi(1)] + 12\sqrt{\pi} - 8\pi$ . The comparatively large values of the correlation length  $\xi$  that are expected to characterize this regime suggest that here  $T_2 \gg T_1$ . For this case, the only acceptable solution to Eq. (33) corresponds to the limit  $l/l_1 \ll 1/l_1$ , where

$$l_1 = (36\mu_0\xi^5B/\pi^2)^{1/3}N^{-1/3}. \quad (35)$$

This result leads to

$$R \sim N^{1/3}. \quad (36)$$

Thus, in this regime, the chain is collapsed.

## V. DISCUSSION

Our calculations show that as the polymer-solvent system approaches the critical point of the solvent, the chain contracts, eventually reaching a compact globular conformation when the correlation length of the solvent density fluctuations is comparable to the mean radial dimensions of the chain, and then re-expands when the correlation length becomes the dominant length scale in the problem. These re-

sults are in complete qualitative accord with data from simulations,<sup>5,8,9</sup> and they match the trends observed in solutions of polymers in near critical bicomponent solvent mixtures.

We interpret the results to mean that the growth of correlations in the medium as the critical point is approached produces a solvent potential of increasingly long range that becomes increasingly effective in screening out excluded volume interactions between different parts of the chain. The effect is strongest when the range of the potential — a screening length, in essence—is on the order of the characteristic dimensions of the chain itself. At much greater distances, however, the effect diminishes, since the dominant solvent fluctuations no longer act on the scale of the polymer, and the original chain dimensions are restored.

The solvent-mediated potential that leads to these results corresponds, in the terminology of field theory and critical phenomena, to a Gaussian approximation;<sup>3</sup> nevertheless, in conjunction with the self-consistent approach of Edwards and Singh, it does appear to be able to produce scaling relations that are decidedly nonclassical. It therefore holds out the possibility of being able to address other problems involving polymers in supercritical fluids. Some of these problems will be the subject of future publications.

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