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# Collapse Transition in Polymers†

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The collapse transition in a single polymer with modified Lennard Jones intersegmental interaction is considered. After defining the appropriate state variables, the equation of state of the system is derived by straightforward statistical mechanics. From approximate numerical solutions for the radial distribution function $g(R)$, it is possible to reproduce the collapse transition observed experimentally.

A long polymer has an expanded form in good solvents, but collapses in a poor solvent. In a single solvent, the polymer chain has its expanded form at high temperatures, but collapses to a globular form at low temperatures. This phenomenon has been observed by recent light scattering experiments on dilute polystyrene solutions by Mazur and McIntyre.[1]

The collapse transition has been studied by Monte Carlo methods on lattice models where the polymer chain has been described as a nonintersecting random walk chain, with a square well attractive potential added between neighbouring units.[2] This transition has also been investigated theoretically by de Gennes[3] by a simple extension of the Flory expression for free energy. De Gennes' approach is largely intuitive. The thermodynamic variables are not clearly defined and the equation of state derived by him is difficult to interpret in terms of the usual equation of state variables—temperature, volume, and pressure. His approach is however valuable in that it reproduces the collapse behaviour and relates this to the tricritical phenomena in magnetic systems.

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In a series of papers[4–6] we have presented the statistical mechanical theory of a single polymer, where we have derived the thermodynamic functions of this system in terms of the radial distribution function $g(R)$.

The formalism, discussed in detail in earlier papers, consists of setting up the configurational partition function of a single polymer and defining appropriate many particle distribution functions. After defining the state variables, volume and tension (analogue of pressure) appropriate to the system, one is able to derive the equation of state in terms of the binary intersegmental potential and $g(R)$. A further consequence of theory was the development of Born–Green–Kirkwood type hierarchy of equations. Detailed numerical computations for $g(R)$ and other thermodynamic potentials were given for a polymer with hard sphere intersegmental interactions, where superposition approximation was used for the computation of $g(R)$. The collapse transition is physically brought about due to the predominance of attractive forces between segments at a critical temperature range. It was, therefore, not found in the hard sphere system. We have now studied the behaviour of a single ring polymer with a modified Lennard Jones intersegmental potential and found the expected collapse transition in this system.

We shall first review briefly the definitions of the state variables. The volume of a single polymer of $N$ segments is defined by

$$V = (\langle S^2 \rangle)^{3/2} = (\langle S^2 \rangle_0)^{3/2} \sigma^3 = V_0 \sigma^3 \tag{1}$$

$$\langle S^2 \rangle_0 = (b^2/12)N \tag{2}$$

where $\langle S^2 \rangle$ is the mean square radius of gyration of the polymer. $\langle S^2 \rangle_0$ is the mean square radius of gyration of noninteracting polymer of $N$ segments with a mean bond length $b$ subject to no internal or external forces. $\sigma^2 = \langle S^2 \rangle / \langle S^2 \rangle_0$ is the expansion coefficient used by Flory and also by de Gennes. Now, it is physically possible to alter $\sigma$ in two independent ways. First the change of temperature in a fixed solvent will result in a change of $\sigma$. Second, at a fixed temperature, one will have different values for $\sigma$ at two different solvents. In good solvents, the solvent molecules generally interpose themselves inside the polymer causing an expansion of the system or an increase in $\sigma$. The solvent thus acts to exert a uniform tension on the polymer system which may be considered to be the physical analogue of the pressure in simple fluids. This tension is now denoted by $\tau$ and is given as the derivative of the free energy, $F$, with respect to volume $V$.

$$\tau = -\frac{1}{V_0}\frac{1}{3\sigma^2}\left(\frac{\partial F}{\partial \sigma}\right)_{T,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{3}$$

Equation of state of the polymer derived by us earlier, gives the relationship between the three variables $\sigma$, temperature $T$, and tension $\tau$.

$$\frac{\beta\tau V}{N} = (1 - \sigma^2) - \frac{2\pi}{3}\beta\int_0^\infty \frac{\mathrm{d}u(R)}{\mathrm{d}R}R^3\rho_0^{(2)}(R:\sigma)g(R:\sigma)\mathrm{d}R \tag{4}$$

Where $g(R;\sigma)$ is the radial distribution function, $\rho_0^{(2)}(R;\sigma)$ the noninteracting pair distribution, $u(R)$ the intersegmental pair potential, and $\beta = 1/kT$. We now choose for $u(R)$ the modified Lennard Jones potential given by

$$u(R) = u_0(R) + u_1(R) \tag{5}$$

$$u_0(R) = \begin{cases} \infty & R \leq a \\ 0 & R > a \end{cases} \tag{6}$$

$$u_1(R) = 0 \qquad R < a \tag{7a}$$

$$u_1(R) = 4\varepsilon\left[\left(\frac{a}{R}\right)^{12} - \left(\frac{a}{R}\right)^6\right] = \varepsilon\gamma(x) \qquad R > a \tag{7b}$$

where $a$ is the hard sphere diameter.

A numerical procedure analogous to the work of Kirkwood, Lewinson and Alder[7] on simple fluids was used to solve for $g(R)$. In this scheme, the $g(R)$ for the polymer with modified Lennard Jones interaction is obtained by a perturbation expansion of the hard sphere radial distribution function in powers of $\beta\varepsilon$

$$g(R:\sigma) = g_0(R:\sigma)[1 + \beta\varepsilon\psi_1(R;\sigma)] \tag{8}$$

where $g_0(R:\sigma)$ and $\psi_1(R:\sigma)$ are the hard sphere radial distribution function and the first term in the perturbation expansion and are given by ($x = R/a$)

$$\ln g_0(x) = \lambda - \frac{\lambda}{4x}\int_{x-1}^{x+1} \mathrm{d}r\, g_0(r)K(r, x) \tag{9}$$

$$K(r, x) = [1 - (x - r)^2 + 2(x + r)(1 - |x - r|)] \tag{10}$$

$$\psi_1(x) = m(x) - \frac{\lambda}{4x}\int_{x-1}^{x+1} \mathrm{d}r\, g_0(r)K(r, x)\psi_1(r) \tag{11}$$

$$\begin{aligned} m(x) = {} & -\gamma(x) + \frac{12}{\sigma^2}\int_1^\infty \mathrm{d}x\, xg_0(x)\gamma(x)\exp\left(-\frac{6x^2}{N\sigma^2}\right) \\ & - \frac{3}{\sigma^2 x}\int_0^\infty \mathrm{d}s\, g_0(s)\gamma(s)\int_{|x-s|}^{x+s} \mathrm{d}r\, g_0(r)(x + r + s) \\ & \times \exp\left[-\frac{3}{2N\sigma^2}(x + r + s)^2 - 4x^2\right] \end{aligned} \tag{12}$$

$\lambda$ is related to $\sigma$ through the thermodynamic identity between chemical potential and tension and its precise form has been given earlier.[6]

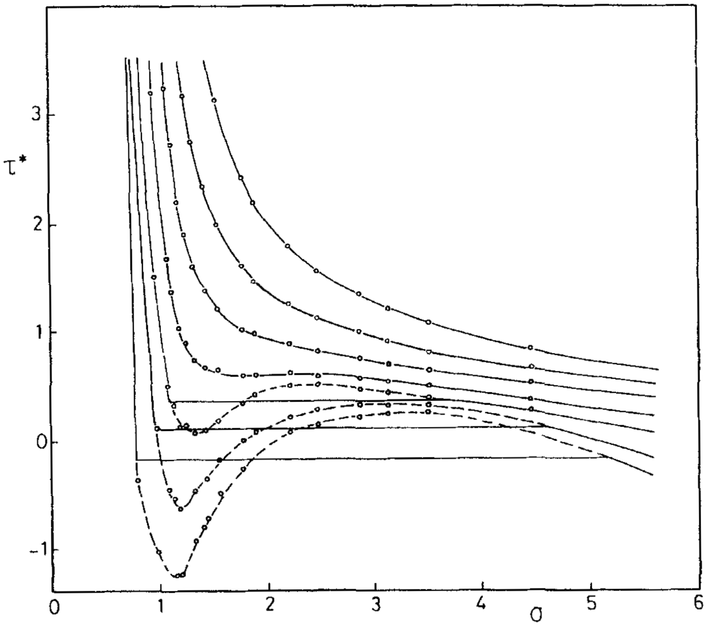

FIGURE 1 Reduced linear tension defined as

$$\tau^* = -\left[\frac{1}{\varepsilon N}\left(\frac{\partial F}{\partial \sigma}\right)_{T,N} - \frac{3\sigma}{\beta\varepsilon}\right]$$

against $\sigma$ for different isotherms $\beta\varepsilon$. Note that $3\sigma/\beta\varepsilon$ is the chain contribution to $\tau^*$.

The system of Eqs. (9)–(12) were solved numerically for different values of the parameter $\lambda$ (different densities). The resulting numerical $g(R)$'s were then substituted in the equation of state (4) and isotherms of Figure 1 were thus obtained.

An alternative method to describe the transition behaviour is to plot $\langle S^2 \rangle$ against $1/T$ at fixed values of tension $\tau$. Such a plot shows more clearly the collapse of the polymer in that below a critical $\tau_c$ (poor solvent) $\langle S^2 \rangle$ rapidly falls off at the collapse temperature. Figure 2 is such a plot for two values of $\tau$. The Monte Carlo work of McCrackin, Mazur and Guttman[2] and the experimental work of Mazur and McIntyre[1] show similar behaviour, but a single curve was obtained by these authors as a single $\tau$ was considered. We have shown that the solvent effect must be such that a tension smaller than critical tension is exerted on the polymer in order for the collapse transition to occur. We have also given precise physical definitions for the state variables of this system.

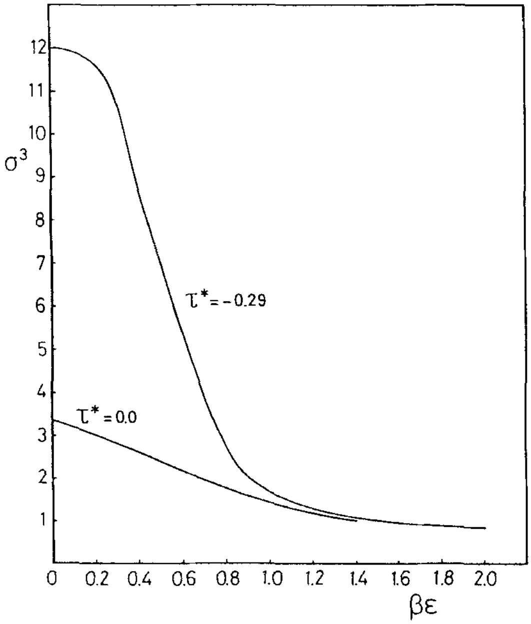

FIGURE 2 $\sigma^3$ vs. inverse reduced temperature $\beta\varepsilon$ for two values of $\tau$. At values of $\tau^* > 0$, no collapse transition is observed.

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