Equation of state of a Lennard-Jones polymer†

J Naghizadeh‡ and N K Ailawadi∥

‡ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 1000 Berlin 33, FDR and Faculty of Sciences, Teheran University, Teheran, Iran
∥ Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 3, 1000 Berlin 33, FDR

Abstract. The equation of state of a single polymer with modified Lennard-Jones intersegmental interaction is considered. From approximate numerical solutions for the radial distribution function $g(r)$, it is possible to study the collapse transition observed experimentally.

In a series of papers we have presented the statistical mechanical theory of a single ring polymer, where we have derived the thermodynamic functions of this system in terms of the radial distribution function $g(r)$ (Naghizadeh 1968, Naghizadeh and Ailawadi 1975a, b).

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 (Naghizadeh 1968). 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 $g(r)$ (Naghizadeh and Ailawadi 1975a). A further consequence of the theory was the development of a Born–Green–Kirkwood-type hierarchy of equations (Naghizadeh 1968). Detailed numerical computations for $g(r)$ and other thermodynamic potentials were given for a polymer with hard-sphere intersegmental interactions (Naghizadeh and Ailawadi 1975b), where the superposition approximation was used for the computation of $g(r)$.

In this paper we discuss the preliminary results for the equation of state of a polymer interacting with a modified Lennard-Jones potential. Attention will be focused on the collapse of the polymer which has been the subject of some recent studies (de Gennes 1975, Mazur and McIntyre 1975, Mazur and McCrackin 1968, McCrackin *et al* 1973).

The volume of a single polymer of N segments is defined by

$$V = R^3 = (\langle R^2 \rangle_0)^{3/2} \alpha^3 \tag{1}$$

wh

$$\langle R^2 \rangle_0 = Nb^2/12, \qquad R = \langle R^2 \rangle_0^{1/2} \alpha \tag{2}$$

where $\langle R^2 \rangle$ is the mean square radius of gyration of the polymer consisting of N segments with a mean bond length b and $\langle R^2 \rangle_0$ is that for a similar polymer but subject to no internal or external forces (non-interacting polymer). $\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0$ is the expansion coefficient used by Flory (1953) and also by de Gennes (1975). Now it is

physically possible to alter α in two independent ways. First the change of temperature in a fixed solvent will result in a change of α. Second, at a fixed temperature, one will have different values of α for 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 α. 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 τ and is given as the derivative of the free energy, F, with respect to volume V.

An equation of state of the polymer derived by us previously (Naghizadeh and Ailawadi 1975a), gives the relationship between the three variables α, temperature T, and tension τ:

$$\frac{\beta \tau V}{N} = (1 - \alpha^2) - \frac{2\pi}{3}\beta \int_0^\infty \frac{du(r)}{dr} r^3 \rho_0^{(2)}(r; \alpha) g(r; \alpha)\, dr. \tag{3}$$

Here $g(r; \alpha)$ is the radial distribution function, $\rho_0^{(2)}(r; \alpha)$ the non-interacting 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

$$u(r) = u_0(r) + u_1(r) \tag{4}$$

$$u_0(r) = \begin{cases} \infty & r \leq a \\ 0 & r > a \end{cases} \tag{5}$$

$$u_1(r) = \begin{cases} 0 & r < a \\ 4\epsilon\left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^6\right] \equiv \epsilon \gamma(r) & r > a \end{cases} \tag{6}$$

where a is the hard-sphere diameter.

A numerical procedure analogous to the work of Kirkwood *et al* (1952) 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 about hard-sphere radial distribution function in powers of $\beta\epsilon$

$$g(r; \alpha) = g_0(r; \alpha)(1 + \beta\epsilon\psi_1(r; \alpha) + \ldots) \tag{7}$$

where $g_0(r; \alpha)$ and $\psi_1(r; \alpha)$ are the hard-sphere radial distribution function and the first term in the perturbation expansion and are given by ($x = r/a$ and $a/b = 1$)

$$\ln g_0(x) = \lambda - \frac{\lambda}{4x}\int_{x-1}^{x+1} dy\, g_0(y)K(y, x) \tag{8}$$

$$K(y, x) = 1 - (x - y)^2 + 2(x + y)(1 - |x - y|) \tag{9}$$

$$\psi_1(x) = m_1(x) - \frac{\lambda}{4x}\int_{x-1}^{x+1} dy\, g_0(y)K(y, x)\psi_1(y) \tag{10}$$

$$m_1(x) = -\gamma(x) + \frac{12}{\alpha^2}\int_1^\infty dx\, x g_0(x)\gamma(x)\exp\left(-\frac{6x^2}{N\alpha^2}\right)$$

$$- \frac{3}{\alpha^2 x}\int_0^\infty ds\, g_0(s)\gamma(s)\int_{|x-s|}^{x+s} dy\, g_0(y)(x + y + s)$$

$$\times \exp\left(-\frac{3}{2N\alpha^2}[(x + y + s)^2 - 4x^2]\right). \tag{11}$$

λ is related to α through the thermodynamic identity between chemical potential and tension τ and its precise form has been given earlier (Naghizadeh and Ailawadi 1975b).

The set of equations (8)–(11) is solved numerically for the pearl-necklace model with $N = 6000$, for different values of the parameter λ corresponding to different densities. Figure 1 shows typical $g(x)$ for one density and two different temperatures.
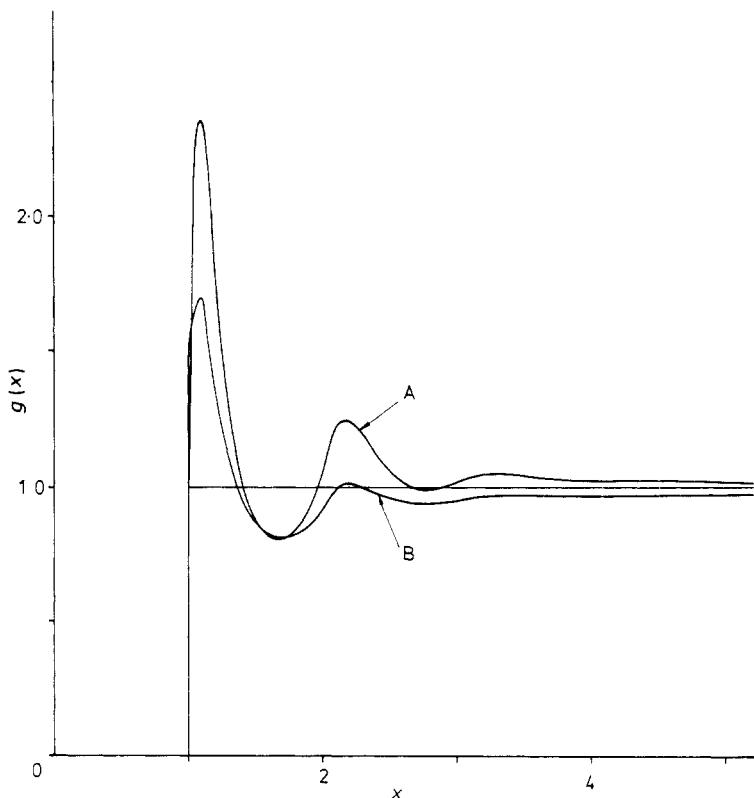

Figure 1. $g(x)$ as a function of x for a density corresponding to $\alpha = 1\cdot29$ with $\lambda = 3\cdot6$ for two different reduced temperatures: A, $\beta\epsilon = 1\cdot2$; B, $\beta\epsilon = 0\cdot4$.

The data obtained in this way are used to calculate the equation of state (equation (3)) and study the collapse of a large polymer in solution. Experimentally, the collapse or gel transition of polymer in a poor solvent has been known for a long time and has been used in polymer fractionation. In traditional polymer chemistry the collapse of the polymer is brought about by a change of solvent, usually by mixing a good solvent and a poor one in various proportions. Recently, the light scattering data of a high molecular weight polystyrene ($\text{MW} = 4\cdot4 \times 10^7$) solution in cyclohexane has been analysed by Mazur and McIntyre (1975).

When the mean square radius of gyration $\langle R^2 \rangle$ for this system is plotted against inverse temperature, it is found that $\langle R^2 \rangle$ rapidly drops by a factor 3 in the neighbourhood of the Θ temperature. Mazur and McCrackin (1968) and McCrackin *et al* (1973) have also studied the temperature dependence of the mean square radius of gyration of a polymer on a lattice with Monte Carlo techniques. Their model polymer was a

self-avoiding polymer on a lattice with a square well attraction for neighbouring segments, not directly bonded together. This model also shows a rapid drop of $\langle R^2 \rangle$ in a critical temperature region.

In the present formalism, it is convenient to rewrite the equation of state (equation (3)) in terms of linear tension τ_L defined by

$$\tau_L = -\left(\frac{\partial F}{\partial R}\right)_{N,T} = -\frac{1}{\langle R^2 \rangle_0^{1/2}}\left(\frac{\partial F}{\partial \alpha}\right)_{N,T}. \tag{12}$$

The linear tension defined above must be distinguished from the earlier definition of tension which was the derivative of the free energy F with respect to V defined in equation (1).

In equation (12) R is equal to $\langle R^2 \rangle^{1/2}$. The present definition of τ_L becomes necessary when comparison with existing polymer literature is to be attempted. The linear tension τ_L has a simple relationship with τ defined earlier, namely

$$\frac{R\tau_L}{3} = \tau V. \tag{13}$$

Further, the reduced linear tension τ_L^* is defined as

$$\tau_L^* = \frac{\tau_L \langle R^2 \rangle_0^{1/2}}{N\epsilon} = -\frac{1}{N\epsilon}\left(\frac{\partial F}{\partial \alpha}\right)_{N,T}. \tag{14}$$

Combining equations (3), (6), (13) and (14), the reduced equation of state takes the dimensionless form

$$\tau_L^* = \frac{3}{\beta\epsilon\alpha} - \frac{3\alpha}{\beta\epsilon} + \frac{2\pi}{\beta\epsilon\alpha^3}\exp\left(-\frac{6}{N\alpha^2}\right)g(\lambda; x = 1)$$

$$-\frac{144}{\alpha^3}\int_1^\infty \left(\frac{1}{x^5} - \frac{2}{x^{11}}\right)g(x;\alpha)\exp\left(-\frac{6x^2}{N\alpha^2}\right)dx. \tag{15}$$

We may now interpret the various terms on the right-hand side of equation (15). The first term $3/\beta\epsilon\alpha$ corresponds to the usual gas term. In the absence of chain connectivity and repulsive and attractive potential terms, this would be the only term which would survive. The second term is due to chain connectivity (or chain elasticity). This is the extra tension exerted on the chain molecules due to their connectivity. The third term is the contribution of repulsive and the fourth that of attractive portions of intersegmental interactions.

We now use equation (15) to plot the τ_L^* against α curves corresponding to the isotherms of the usual P–V diagrams in simple fluids. Note, however, that the transition is brought about by a competition between repulsive and attractive potential terms and the *net tension* exerted on the particles. We may now consider the system as being composed of free particles upon which two types of confining forces are operating. The first confining force is that due to τ_L^* which simulates the solvent action and the second is $3\alpha/\beta\epsilon$, which is the confining force due to chain connectivity. The *net force* tending to confine the particles is the sum of these two. In figure 2 the net tension $[\tau_L^* + (3\sigma/\beta\epsilon)]$ is plotted against the reduced linear extension α for various values of the inverse reduced temperature $\beta\epsilon$. One notes that the usual van der Waals loops are
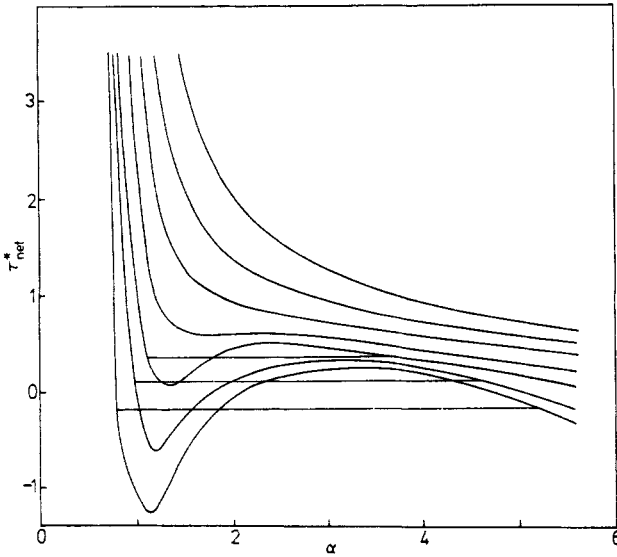
Figure 2. Reduced net tension defined as

$$\tau_{net}^{*} = \tau_{L}^{*} + \frac{3\alpha}{\beta\epsilon} = -\frac{1}{N\epsilon}\left(\frac{\partial F}{\partial\alpha}\right)_{N,T} + \frac{3\alpha}{\beta\epsilon}$$

against α. Note that $3\alpha/\beta\epsilon$ is the chain contribution to τ_{L}^{*}.

obtained as expected. The two-phase behaviour sets in at values of reduced inverse temperature $\beta\epsilon > 1\cdot2$. Thus a critical temperature and critical tension exist in this system as in the analogous simple fluid case.

Recently, de Gennes (1975) has presented a simple theory for a collapse transition in polymers using a modified Flory expression for the free energy. Minimization of this free energy with respect to α leads to

$$-\frac{y}{\alpha^{7}} = \frac{1}{\alpha} - \alpha + \frac{x}{\alpha^{4}}. \tag{16}$$

A plot of α against x for different values of y produces transition behaviour similar to magnetic transitions at the tricritical point. To compare our theory with de Gennes', we note that in the equation of state (15) the sum of the two terms due to the repulsive and attractive parts of the potential corresponds to the x term of equation (16). These terms involve a factor $1/\alpha^{3}$. An examination of data for $g(x)$ shows that g is inversely related to the expansion coefficient α. Bearing this in mind, the two equations (15) and (16) have similar structures in the parameter α. The precise α and N dependence of τ_{L}^{*} and g are not clear, and therefore a better comparison cannot be made at this time. The parameter y in de Gennes' work arises from the third virial term added to the Flory free energy expression. This term may possibly be related to the reduced tension τ_{L}^{*} in our theory.

De Gennes' theory, however, needs to be re-examined in the light of a recent work by des Cloizeaux (1976) which shows that the Flory term is absent in the free energy expression for a polymer.

References

des Cloizeaux J 1976 *J. Physique* **37** 431
Flory P J 1953 *Principles of Polymer Chemistry* (Ithaca, NY: Cornell University Press) chap. 14
de Gennes P G 1975 *J. Physique Lett.* **36** L55
Kirkwood J G, Lewinson V A and Alder B J 1952 *J. Chem. Phys.* **20** 929
Mazur J and McCrackin F L 1968 *J. Chem. Phys.* **49** 648
Mazur J and McIntyre D 1975 *Macromolecules* **8** 464
McCrackin F L, Mazur J and Guttman C M 1973 *Macromolecules* **6** 859
Naghizadeh J 1968 *J. Chem. Phys.* **48** 1961
Naghizadeh J and Ailawadi N K 1975a *J. Chem. Phys.* **63** 650
—— 1975b *J. Chem. Phys.* **63** 657