

## **A Continuum Analysis of a System of Many 'Real' Chains Confined Between a Pair of 'Sticky' Surfaces, with Application to the 'Sandwich' Model of Bulk Polymers**

**Richard J. Gaylord and Young Hwa Kim**

The Polymer Group, Department of Metallurgy and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

### SUMMARY

An analysis is made of a system of many interacting chains confined between a pair of surfaces which exert a short range attraction on the chains. The free energy of the system is determined from the partition functions of the confined chains which are, in turn, determined by solutions to the self consistent field form of the diffusion equation with mixed boundary conditions. The incorporation of the analysis into the 'sandwich' model of bulk polymers is discussed.

### I. INTRODUCTION

A theoretical study of a system comprised of many interacting 'real' chains (ie., chains with excluded volume interactions between the chain segments) which are confined between a pair of infinite, parallel 'sticky' surfaces (ie., surfaces which have a short range interaction with the chain segments) is useful because this system can serve as a model for: the steric stabilization of colloids (DOLAN and EDWARDS 1975, GERBER and MOORE 1977, JOANNY, et al., 1979), the amorphous component in bulk polymeric systems (GAYLORD et al. 1980b), adhesion, and the formation of a shish structure during strain-induced polymer crystallization.

In the following sections, we will examine this system using a continuum method based on solutions of the self consistent field form of the diffusion equation which satisfy mixed boundary conditions. We will first set up the appropriate mathematical formulas. Then, we will derive the mathematical expressions for the partition function of a chain in the system and the total free energy of the system. Finally, we will discuss the application of the method to the 'sandwich' model of bulk polymers (GAYLORD et al. 1980b).

### II. THE MATHEMATICAL FORMULATION OF THE PROBLEM

Our system is comprised of many 'real' chains between a pair of 'sticky' surfaces. The total segment concentration is taken to

be sufficiently large so that: (1) the system will have translational invariance in directions which are parallel to the surfaces, thereby permitting us to perform our mathematical analysis in one dimension in the direction which is normal to the surfaces, and (2) the fluctuations in the overall segment density will be relatively small, thereby enabling us to treat the segment-segment interactions as an external, self consistent field acting on independent chains.

The partition function of a real polymer chain consisting of  $N$  segments, each of length  $b$ , having its ends located at  $x, x'$  and being confined with many other 'real' chains, between a pair of 'sticky' surfaces a distance  $d$  apart, is given (DOLAN and EDWARDS 1975, GAYLORD et al. 1980b) by the solution to the set of equations

$$[\partial/\partial N - (b^2/6)\partial^2/\partial x^2 + \nu\rho_T(x)] G(N, x, x') = b\delta(x-x')\delta(N) \quad (1)$$

$$\partial \ln G(N, x, x')/\partial x|_{x=0} = \sigma \quad (2)$$

$$\partial \ln G(N, x, x')/\partial x|_{x=d} = -\sigma \quad (3)$$

where  $\nu \sim (1/2 - \chi)$  is the Flory excluded volume parameter,  $\rho_T(x)$  is the total segment density at a distance  $x$  from one of the surfaces and  $\sigma$  is a parameter which represents the segment-surface attraction (while it is not possible to use a continuum analysis to establish a quantitative relationship between  $\sigma$  and the form of the segment-surface potential (DEGENNES 1979), we can say that as  $\sigma$  becomes less positive (or more negative), the segment-surface attraction becomes greater).

Equations (1) - (3) are equivalent to (WEIGEL 1975).

$$G(N, x, x') = G^0(N, x, x') \left\{ 1 - \int_0^d dx'' \nu \rho_T(x'') \cdot \int_0^N dm [G^0(m, x, x'') G(N-m, x'' x') / G^0(N, x, x')] \right\} \quad (4)$$

where  $G^0(N, x, x')$  is given by the solution to the set of equations

$$[\partial/\partial N - (b^2/6)\partial^2/\partial x^2] G^0(N, x, x') = b\delta(x-x')\delta(N) \quad (5)$$

$$\partial \ln G^0(N, x, x')/\partial x|_{x=0} = \sigma \quad (6)$$

$$\partial \ln G^0(N, x, x')/\partial x|_{x=d} = -\sigma \quad (7)$$

### III. THE SOLUTION TO EQUATIONS (1) - (3) USING THE GROUND STATE APPROXIMATION TO THE EIGENFUNCTION EXPANSION METHOD SOLUTION

When the surface separation,  $d$ , is less than the root-mean-square, end-to-end separation of the chain,  $(Nb^2)^{1/2}$ , we can approximate equation (1) - (3) by (DEGENNES 1979, DEGENNES 1969)

$$G(N, x, x') \approx u(x) u(x') \exp(-\epsilon N) \quad (8)$$

where  $\epsilon$  and  $u(x)$  are the ground state eigenvalue and eigenfunction of the set of equations

$$-(b^2/6)d^2u(x)/dx^2 + v\rho_T(x)u(x) = \epsilon u(x) \quad (9)$$

$$d \ln u(x)/dx|_{x=0} = \sigma \quad (10)$$

$$d \ln u(x)/dx|_{x=d} = -\sigma \quad (11)$$

The segment density profile of a chain which is characterized by equation (8) is given by (DEGENNES 1979)

$$\rho(x) = N u^2(x) \quad (12)$$

As equation (12) indicates, the segment density profile of the chain is not dependent on the location of the chain ends (this is because the ground state approximation assumes the  $d^2 < Nb^2$ ). The mixed boundary condition parameter  $\sigma$  represents the short range segment-surface interaction, and it should be related to the segment density profile. Therefore, since all of the chain types (cilia, bridges, floating chains and loops) have the same form of  $\rho(x)$  in the ground state approximation, they should also have the same value of  $\sigma$  in the ground state approximation. Therefore,  $\rho_T(x)$ , which is the sum of the segment density profiles of all the chains in the system,

$$\rho_T(x) = \sum_i \rho_i(x) \quad (13)$$

becomes

$$\rho_T(x) = N_T u^2(x) \quad (14)$$

where  $N_T$  is the total number of chain segments in the system. The solution to equations (9) - (11), (14) is given by

$$u(x) = a \operatorname{sn}[(x/B) + R, m] \quad (15)$$

where  $\operatorname{sn}$  denotes the Jacobian elliptic function and

$$a = \{[\epsilon - (\epsilon^2 - 4vN_T c)^{1/2}] / vN_T\}^{1/2}$$

$$B = \{b^2[\epsilon - (\epsilon^2 - 4vN_T c)^{1/2}] / (12vN_T c)\}^{1/2}$$

$$c = [(b^2 \sigma^2 / 12) + (\epsilon/2)] u^2(x=0) - [vN_T / 4] u^4(x=0)$$

$$m = [\epsilon - (\epsilon^2 - 4vN_T c)^{1/2}] / [\epsilon + (\epsilon^2 - 4vN_T c)^{1/2}]$$

The quantities  $R$  and  $u(x=0)$  are determined by

$$\int_0^d u^2(x) dx = 1$$

and

$$d u(x)/dx|_{x=d/2}=0$$

Equation (15) can be used in conjunction with equation (8) to calculate the chain partition function. However there are some drawbacks to using this ground state approximation method: (1) the numerical evaluation of equation (15) is difficult, (2) the requirement that the segment-surface attraction be the same for all chains in the system prevents its use in the sandwich model (GAYLORD et al. 1980b), and (3) the requirement that the contour length of the chain be much greater than the surface separation prevents its use in the analysis of tight loops or taut bridges. For these reasons, we will not pursue this method further and will turn to an alternative, albeit approximate, method for analyzing the system.

#### IV. A PERTURBATION EXPANSION OF EQUATION (4)

If we examine equation (4), we see that the leading term in the factor  $G(N-m, x, x')$  has the form  $G^0(N-m, x, x')$ . Substituting this term into equation (4) yields the approximate expression

$$G(N, x, x') \approx G^0(N, x, x') \{1 - v \int_0^d dx'' \rho_T(x'') \rho^0(x'') + \dots\} \quad (16)$$

where

$$\rho^0(x'') = \int_0^N dm [G^0(m, x, x'') G^0(N-m, x'', x') / G^0(N, x, x')] \quad (17)$$

We now assume that the segment density profile of a chain in the system is not appreciably affected by excluded volume interactions (this is acceptable in the range within which equations (1), (4) and (16) are valid (DOLAN and EDWARDS 1975, HESSELINK, 1977)). This assumption can be expressed by rewriting equation (13) as

$$\rho_T(x'') = \sum_i \rho_i^0(x'') \quad (18)$$

In order to use equations (16) - (18), we need an expression for  $G^0(N, x, x')$ . This is obtained by solving equations (5) - (7). The results are given in the next two sections.

#### V. THE SOLUTION FOR $G^0(N, x, x')$ BY THE EIGENFUNCTION EXPANSION METHOD

This solution is well known (CARSLAW and JAEGER 1959). The result is

$$G^0(N, x, x') = \sum_{p=1}^{\infty} 2[\alpha_p \cos(\alpha_p x) + \sigma \sin(\alpha_p x)][\alpha_p \cos(\alpha_p x') + \sigma \sin(\alpha_p x')] \cdot \exp(-\alpha_p N b^2 / 6) / [d(\alpha_p^2 + \sigma^2) + 2\sigma] \quad (19)$$

where the  $\alpha_p$ ;  $p = 1, 2, \dots$  are the roots of the

transcendental equation

$$\tan(\alpha d) = 2\sigma\alpha/(\alpha^2 - \sigma^2) \quad (20)$$

(We note that for  $\sigma=0$ , it is necessary to add the term  $(1/d)$  to equation (19)).

The chief difficulty in using equation (19) is that it requires a graphical solution of equation (20). For this reason, we have developed an alternative expression for  $G^0(N, x, x')$ , which does not include a transcendental equation.

#### VI. THE SOLUTION FOR $G^0(N, x, x')$ BY THE LAPLACE TRANSFORM METHOD

We first Laplace transform equations (5) - (7) with respect to  $N$ . This gives

$$d^2 f/dx^2 - (6s/b^2)f = (-6/b^2) \delta(x-x') \quad (21)$$

$$d \ln f/dx|_{x=0} = \sigma \quad (22)$$

$$d \ln f/dx|_{x=d} = -\sigma \quad (23)$$

Solving equations (21) - (23) and then taking the inverse Laplace transform yields<sup>1/2</sup>

$$\begin{aligned} G^0(N, x, x') &= \{(nb^2/\pi)^{1/2} \exp[-n(x-x')^2]\} \\ &+ \left[ \sum_{\ell=1}^{\infty} (nb^2/\pi)^{1/2} \{ \exp[-n(2d\ell-2d+x'+x)^2] \} + \exp[-n(2d\ell-x'-x)^2] \right. \\ &\quad \left. + \exp[-n(2d\ell+x'-x)^2] + \exp[-n(2d\ell-x'+x)^2] \right] \\ &- \left[ \sum_{\ell=1}^{\infty} b [2(2\ell-2)!]^{-1} \sum_{q=0}^{2\ell-1} \{ [2\ell-1]!/q!(2\ell-1-q)! \} \sigma^{2\ell-1-q} \right. \\ &\quad \cdot \partial^{2\ell-2}/\partial\sigma^{2\ell-2} (\sigma^q \exp(\sigma^2/4n) \{ \exp[\sigma(2d\ell-2d+x+x')] \} \\ &\quad \cdot \operatorname{erfc}[\{(\sigma/2n)+2d\ell-2d+x+x'\}n^{1/2}] + \exp[\sigma(2d\ell-x'-x)] \\ &\quad \cdot \operatorname{erfc}[\{(\sigma/2n)+2d\ell-x'-x\}n^{1/2}]\} \} - \left[ \sum_{\ell=1}^{\infty} b [2(2\ell-1)!]^{-1} \right. \\ &\quad \cdot \sum_{q=0}^{2\ell} \{ [(2\ell)!/q!(2\ell-q)!] \sigma^{2\ell-q} \partial^{2\ell-1}/\partial\sigma^{2\ell-1} (\sigma^q \exp(\sigma^2/4n) \\ &\quad \cdot \{ \exp[\sigma(2d\ell-x'+x)] \operatorname{erfc}[\{(\sigma/2n)+2d\ell-x'+x\}n^{1/2}] \} \end{aligned}$$

$$+ \exp[\sigma(2d\lambda+x'-x)] \operatorname{erfc}[(\sigma/2n)+2d\lambda+x'-x)n^{1/2}]] \} \} \quad (24)$$

where  $n = (3/2Nb^2)$ .

### VII. THE TOTAL FREE ENERGY OF THE SYSTEM

As noted in section II, the use of the self consistent field potential 'decouples' the chains and permits us to treat them as independent. The total free energy of the system is therefore given by using equations (16) - (18) and summing over all chains in the system to produce

$$A_T = -kT \sum_i \ln G_i^0 + \frac{\nu kT}{2} \int_0^d dx \left[ \sum_i \rho_i^0(x) \right]^2 \quad (25)$$

The factor 1/2 is introduced into the second term to account for double counting of segment-segment interactions.

### VIII. APPLICATION TO THE 'SANDWICH' MODEL

The sandwich model (GAYLORD et al. 1980b) consists of a system of  $M_B$  bridges with  $N_B$  segments each,  $M_C$  cilia with  $N_C$  segments each,  $M_L$  loops with  $N_L$  segments each and  $M_F$  floating chains with  $N_F$  segments each, between two infinite parallel 'sticky' surfaces which are a distance  $d$  apart. The total free energy of the system is given, using equation (25) by

$$A_T = -kT \sum_{j=C,L,B,F} M_j \ln G_j^0(d, \sigma_j, N_j) + \frac{\nu kT}{2} \int_0^d dx \left[ \sum_{j=C,L,B,F} M_j \rho_j^0(x, d, \sigma_j, N_j) \right]^2 \quad (26)$$

where each chain type  $j$  is assigned a unique  $\sigma_j$ . We can calculate  $G_j^0, \rho_j^0$  for each chain type by using equations (19) and (20) or equation (24), together with formulas given elsewhere (GAYLORD et al. 1980a).

In order to determine the  $\sigma_j$  values, we minimize  $A_T$  with respect to each of the  $\sigma_j$  subject to the constraint of a uniform segment density between the surfaces. We therefore solve the set of equations

$$0 = \frac{\partial}{\partial \sigma_j} \{ A_T + \lambda \sum_{j=C,L,B,F} M_j \rho_j^0(x) \} \text{ for all } j \quad (27)$$

where  $\lambda$  is a Lagrange multiplier. The solutions to these equations give us the  $\sigma_j^*$  values for each chain type and these  $\sigma_j^*$  will be functions of  $d$ ,  $\lambda$ ,  $N_j$  and  $M_j$  for all  $j, v$ . Substituting these  $\sigma_j^*$  into our  $\rho_j^0$  expressions and using the equation of constraint,  $\sum_j M_j \rho_j^0(x) = N_T/d$ , we then obtain  $\lambda$  as a function of  $d$ ,  $N_j$  and  $M_j$  for all  $j, v$ . Thus, we are able to obtain  $A_T$  as a function of only  $d$ ,  $N_j$  and  $M_j$  for all  $j, v$ . We are now able to calculate both the swelling and the deformation properties of the 'sandwich' model. Since the total segment density profile in the 'sandwich' model is taken to be uniform prior to deformation, it should remain uniform during at least the initial stages of swelling or deformation. Therefore, all that we need to know are the relationships between the surface separation,  $d$ , of the model, the specific type of deformation, and the particular bulk polymeric system being considered. This can be done using some primitive models which have recently been developed (GAYLORD 1979a, GAYLORD 1979b, LOHSE and GAYLORD 1978b, GAYLORD and LOHSE 1978a) to describe the deformation and swelling behavior of the amorphous regions in semicrystalline polymers, block copolymers and filled or reinforced elastomers. (These models were developed incorrectly before (GAYLORD 1979b, LOHSE and GAYLORD 1978, GAYLORD and LOHSE 1978) because (i) they did not produce a uniform segment density profile, and (ii) they used, without justification, absorbing boundary conditions ( $\sigma = \infty$ ) in calculating the free energies of the confined chains (LOHSE and GAYLORD 1977, GAYLORD AND LOHSE, 1976). The 'sandwich' model avoids these failings.)

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