

A NEW MODEL FOR THE SWELLING OF COAL

Paul C. Painter and Suresh L. Shenoy
Polymer Science Program
Penn State University
University Park, PA 16802

Key Words: Coal swelling, molecular weight, hydrogen bonding

INTRODUCTION

Most studies of the swelling of coal have been based on the Flory-Rehner model for the swelling of polymer networks, sometimes modified to account for factors such as finite chain length, or in work conducted in this laboratory, hydrogen bonding interactions. However, as a result of work reported over the last ten years or so (e.g., references 1-5) it is now clear that there is a big problem with this approach. Although some data has been interpreted so as to bring in to question the fundamental assumption of the separability of the elastic and free energies (6,7), the most serious deficiency appears to be the second major assumption of the Flory-Rehner theory, that the deformation of the elementary chains of the network is in some fashion affine with the macroscopic deformation (swelling) of the sample. The neutron scattering work of Bastide et al. (3) has demonstrated that the network elementary chains have approximately the same dimensions as equivalent non cross-linked chains in solutions of the same concentration, which is much less than would be expected on the basis of an affine deformation model. These results are in good agreement with the c^* theorem of de Gennes (8), who proposed that in a good solvent the swollen coils of the network largely exclude one another from a volume that is (more-or-less) defined by their radius of gyration, but because the chains are forced into contact at their cross-link points the gel is analogous to the situation at the overlap threshold in a semi-dilute solution. Accordingly, Bastide et al. (2) proposed that the swelling of a gel proceeds by a process of topological rearrangement or disinterspersion of the cross-link points or nodules and demonstrated that an analysis based on a scaling approach is in good agreement with experimental observations.

In recent work we have modified the classical Flory-Rehner approach by abandoning the affine assumption (9). We have used the packing conditions that are a consequence of the c^* theorem and a scaling law to define a relationship between the degree of swelling and elementary chain extension. The model appears to provide a good description of various swelling and deswelling experiments and provides a simple foundation on which we can examine the swelling of coal. We can only report here an outline of the model and the theory will be presented in greater detail in a separate publication. We will consider first the basic equations for the free energy, then consider how these must be modified to account for two crucial features of coal structure, hydrogen bonding and finite chain length.

THEORY AND CALCULATIONS

We start with a hypothetical perfect network of very long chains, each of the same length (degree of polymerization, N) and cross-link functionality (f). The treatment for equilibrium swelling in a good solvent where the swollen chains are at the threshold between the dilute and semi-dilute regimes is straightforward and uses three basic and familiar assumptions:

- 1) The free energy of the gel can be written as the sum of two separate components, describing the elastic free energy and mixing free energy, respectively.
- 2) These components of the free energy can be expressed in terms of the classic elastic free energy and the Flory-Huggins theory (modified later to account for hydrogen bonding).
- 3) Following de Gennes, we assume that *at equilibrium in a good solvent* the chains expand to the extent that they would in a dilute solution of the same solvent. The cross link points

disintersperse to the extent that the gel is a collection of spheres of individual network chains that as far as possible exclude segments of other chains from their volume, but are forced into contact at their cross-link points, as illustrated in figure 1.

Using the first two assumptions the equations for the free energy can be written down immediately, while the final assumption provides the essential connection between the volume fraction of polymer segments (i.e., the degree of swelling) and the chain expansion factor (9). The free energy is then given by:

$$\frac{\Delta F}{RT} = v \left[\frac{3}{2} (\alpha^2 - 1) - \ln \alpha^3 \right] - \xi \ln \phi_c + n_s \ln (1 - \phi_c) + n_s \phi_c \chi \quad (1)$$

where n_s is the number of moles of solvent, ϕ_s , ϕ_c are the volume fractions of coal and solvent, respectively ξ is the cycle rank of the network, v is the number of chains, χ is the Flory-Huggins interaction parameter and α is the chain expansion factor. The chemical potential of the solvent then follows immediately as:

$$\frac{\Delta \mu_s}{RT} = - \left[3v \left(\alpha - \frac{1}{\alpha} \right) \frac{\phi_c^2}{Nv} \right] \frac{\partial \alpha}{\partial \phi_c} + \frac{\xi \phi_c}{Nv} + \ln (1 - \phi_c) + \phi_c + \phi_c^2 \chi \quad (2)$$

In models that assume an affine deformation an expression for $\partial \alpha / \partial \phi_c$ is obtained from the condition $\phi_c = 1/\alpha^3$. In using the c^* model we can obtain a similar relationship from the packing condition (9):

$$\phi_c' = \frac{1}{\alpha^3 N^{1/2}} \quad (3)$$

where ϕ_c' is the volume fraction of coal segments within *each excluded volume domain* or "blob". For highly swollen networks ϕ_c' is not the same as the overall or nominal concentration ϕ_c , but we have calculated that for degrees of swelling less than 5 the packing factor that connects these two quantities is about 1 (9), so for coal, where the degrees of swelling are usually of the order of 2-3 we obtain

$$\frac{\Delta \mu_s}{RT} = \frac{\phi_c^{1/3}}{N^{4/3}} - \left(1 - \frac{\xi}{v} \right) \frac{\phi_c}{N} + \ln (1 - \phi_c) + \phi_c + \phi_c^2 \chi \quad (4)$$

This is very similar in form to the Flory-Rehner result, differing only in the first term, where the assumption of an affine deformation results in a $\phi_c^{1/3}/N$ term.

THE EFFECT OF HYDROGEN BONDING AND FINITE CHAIN LENGTH

The method we have used to describe hydrogen bonding interactions depends upon the determination of the modification to the number of configurations available to the chains when they are required to form their equilibrium distribution of hydrogen bonds, relative to the state where the chains are not hydrogen bonded at all. The details of this procedure have been presented elsewhere (10,11) and its initial application to coal has also been discussed (12). We will not reproduce the equations here but simply note that this introduces an extra term, $\Delta \mu_H/RT$, into equation 4, where the contributions of hydrogen bonds to the solvent chemical potential can be calculated from equilibrium constants that, in turn, can be experimentally determined using infrared spectroscopy (11).

The effect of finite chain length is less easily handled. Previously we used a model developed by Kovac (13) and first applied to coal by Larsen et al. (14). Here we will confine our calculations to a simpler approach. Flory (15) compared approximate distribution functions to an exact expression and

found for short chains (e.g., $N=4$) at small extensions the Gaussian function was the best approximation, but at higher extensions an inverse Langevin distribution (which Flory preferred to call the L^* distribution) was superior. In initial calculations we have found that strong specific interactions are a strong driving force for chain expansion, so we will employ both approximations and compare the results. In the Gaussian approximation we employ equation 4 with the added hydrogen bonding contribution, while the use of the L^* distribution gives:

$$\begin{aligned} \frac{\Delta\mu_z}{RT} = & \left[1 + \frac{3}{5}\alpha^2 + \frac{(11)(27)}{(2)(175)}\alpha^4 \right] \frac{\alpha^2\phi_c}{N} \\ & - \left[\frac{1}{1 + \frac{3}{5}\alpha^2 + \frac{(33)(9)}{(2)(175)}\alpha^4} \right] \left[\frac{2}{5} + \frac{(2)(99)}{175}\alpha^2 \right] \frac{\alpha^2\phi_c}{N} \\ & - \frac{\phi_c}{N} \left(1 + \frac{\xi}{v} \right) + \ln(1 - \phi_c) + \phi_c + \phi_c^2 \chi + \frac{\Delta\mu_H}{RT} \end{aligned} \quad (5)$$

where the L^* distribution has been truncated after the α^4 term.

The results of applying these equations are shown in figures 2 and 3, which shows a plot of the chemical potential as a function of the concentration of coal in the swollen sample. The non-zero intercept corresponds to the reciprocal of the degree of swelling. Calculations were performed using parameters for an Illinois #6 coal swollen in pyridine and THF, as listed in reference 12. We employed the data for swelling in pyridine ($Q=2.5$ or $\phi_c=0.4$) to calculate the number of statistical units in a chain, and it can be seen that we calculate a value of $N=2$ for the Gaussian approximation and $N=4$ using the L^* distribution. The number of "aromatic clusters" per statistical unit is probably of the order of 5-10 (a statistical unit consists of a sufficient number of segments to give behavior equivalent to that of a freely jointed chain), so that the average number of units between cross link points is probably of the order of 20, if the model is correct.

One test of the validity of the model is the degree to which it can now predict other results. Also shown in figure 2 are calculations of the chemical potential of Illinois #6 coal swollen in THF. Because this solvent hydrogen bonds less strongly than pyridine the driving force for chain expansion is less, so we calculate an equilibrium value of ϕ_c of the order of 0.5, or a degree of swelling $Q=2$. This is in good agreement with experiment (14).

ACKNOWLEDGMENT

We gratefully acknowledge the support of the Office of Basic Energy Sciences, Division of Chemical Sciences, Department of Energy, under Grant no. DE-FG02-86ER13537.

REFERENCES

1. Bastide, J., Candau, S., and Leibler, L., *Macromolecules*, 1981, 14, 719.
2. Bastide, J., Picot, C. and Candau, S. J., *Macromol. Sci., Phys.*, 1981, B19, 13.
3. Bastide, J., Duplessix, R., Picot, C. and Candau, S., *Macromolecules*, 1984, 17, 83.
4. Horkay, F. and Zrinyi, M., in "Biological and Synthetic Polymer Networks", Edited by O. Kramer, Elsevier Applied Science, 1988.

5. Geissler, E., Hecht, M., Horkay, F., and Zrinyi, M., in "Springer Proceedings in Physics", Vol. 42, Edited by Baugartner, A. and Picot, C. E., 1989.
6. Neuberger, N. A. and Eichinger, B. E., *Macromolecules*, 1988, 21, 3060.
7. McKenna, G. B., Flynn, K. M. and Chen, Y. H., *Polymer Communications*, 1988, 29, 272.
8. de Gennes, P. G., "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, 1979.
9. Painter, P. C. and Shenoy, S. L., *J. Chem. Phys.* (In Press).
10. Painter, P. C., and Graf, J. and Coleman, M. M., *J. Chem. Phys.*, 1990, 92, 6166.
11. Coleman, M. M., Graf, J. and Painter, P. C., "Specific Interactions and the Miscibility of Polymer Blends", Technomics, Lancaster, PA 1991.
12. Painter, P. C., Park, Y., Sobkowiak, M., and Coleman, M. M., *Energy and Fuels*, 1990, 4, 384.
13. Kovac, J., *Macromolecules*, 1978, 11, 362.
14. Larsen, J. W., Green, T., Kovac, J., *J. Org. Chem.*, 1985, 50, 4729.
15. Flory, P. J., *Statistical Mechanics of Chain Molecules*, Hanser Publishers, Reprinted Edition, 1989.

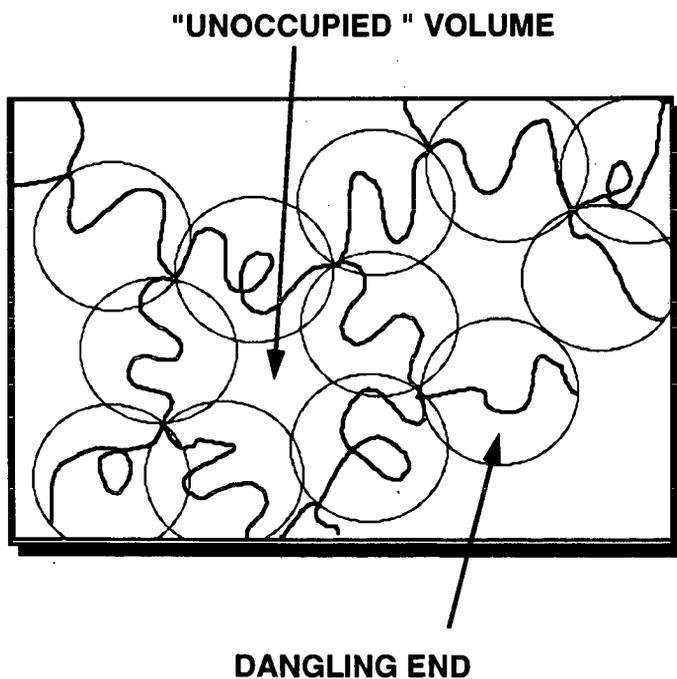
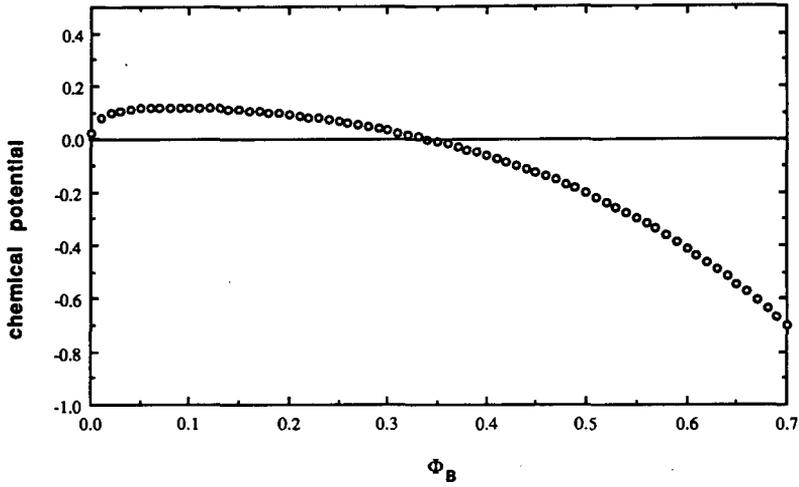


Figure 1. Pictorial representation of the C^* model of a swollen network

Illinois#6/pyridine n=2 (gaussian)



Illinois#6/thf n=2 (gaussian)

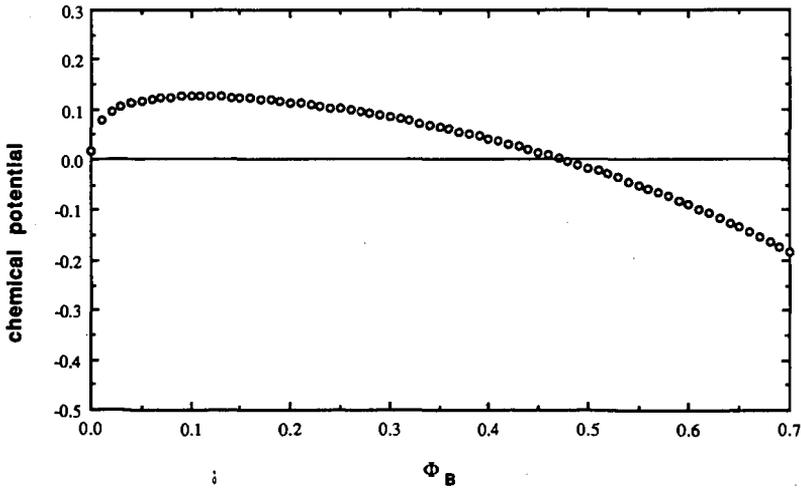
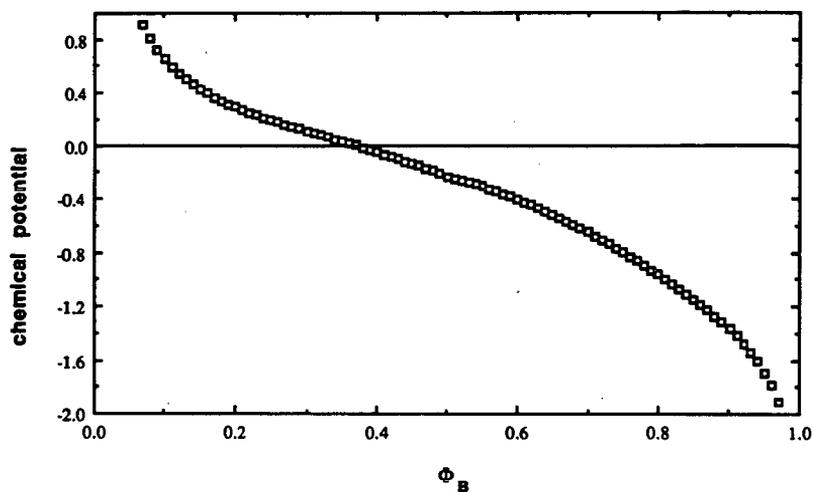


Figure 2. Calculation of the chemical potential as a function of coal segment concentration (Φ_B) in using the Gaussian approximation. Top: Illinois#6 coal swollen in pyridine; Bottom: swollen in THF

Illinois#6/pyridine n=4 (non gaussian)



Illinois#6/thf n=4 (non gaussian)

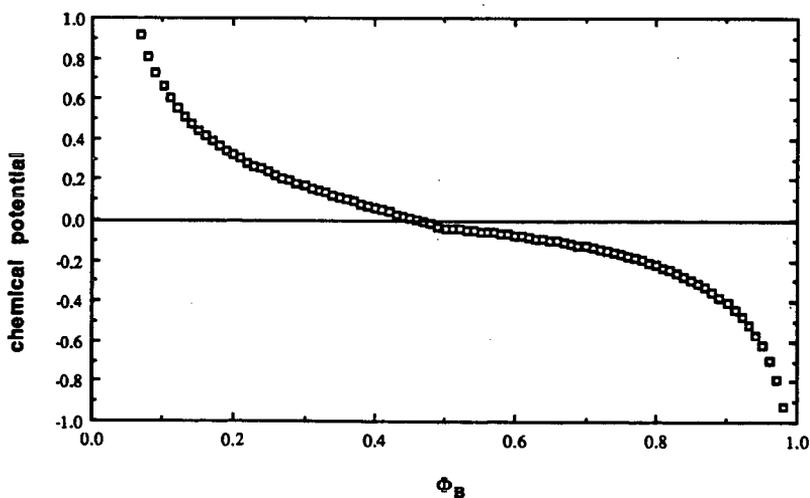


Figure 3. Calculation of the chemical potential as a function of coal segment concentration (ϕ_B) using the L* distribution. Top: swollen in pyridine; Bottom: swollen in THF