3172 *Macromolecules* 1990, *23*, 3172–3178

(14) Guttmann, A. J. *J. Phys. A: Math. Gen.* **1987**, *20*, 1839.
(15) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561.
(16) Olaj, O. F.; Zifferer, G., to be submitted for publication.
(17) Kranbuehl, D. E.; Verdier, P. H. *J. Chem. Phys.* **1972**, *56*, 3145.
(18) Meirovitch, H. *Macromolecules* **1984**, *17*, 2038.
(19) Müller-Krumbhaar, H.; Binder, K. *J. of Stat. Phys.* **1973**, *8*, 1.
(20) Friedberg, R.; Cameron, J. E. *J. Chem. Phys.* **1970**, *52*, 6049.
(21) Schiferl, S. K.; Wallace, D. C. *J. Chem. Phys.* **1985**, *83*, 5203.
(22) Straatsma, T. P.; Berendsen, H. J. C.; Stam, A. J. *Mol. Phys.* **1986**, *57*, 89.
(23) Bishop, M.; Frinks, S. *J. Chem. Phys.* **1987**, *87*, 3675.
(24) Flyvbjerg, H.; Petersen, H. G. *J. Chem. Phys.* **1989**, *91*, 461.
(25) Feller, W. *An Introduction to Probability Theory and its Applications*; Wiley: New York, 1968.
(26) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(27) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987.
(28) Le Guillou, J. C.; Zinn-Justin, J. *J. Phys. Rev. B* **1980**, *21*, 3976.
(29) Lowry, G. G. *Markov Chains and Monte Carlo Calculations in Polymer Science*; Marcel Dekker: New York, 1970; papers cited in refs 1 and 2.

# Screening of Interactions in Homopolymer Blends and in Diblock Copolymer Systems

**T. A. Vilgis* and R. Borsali**

*Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, FRG*

*Received September 11, 1989; Revised Manuscript Received December 5, 1989*

ABSTRACT: The screening of interactions is compatible binary homopolymer blends A and B and in the diblock copolymer A–B system is studied. A systematic comparison between both cases is presented, and a general expression for the effective screened potential $U_{AA}{}^{s}$, acting on one chain of type A, is given as a function of the compositions $\Phi_A$ and $\Phi_B$ for both components, their Flory interaction parameter $\chi_F$, the degrees of polymerization $N_A$ and $N_B$, and the wave vector $|\mathbf{k}|$. The theoretical variation of the screened potential $U_{AA}{}^{s}$ as a function of the composition and the wave vector is considered in the case of homopolymer blends A and B and in the case of the diblock copolymer system. The main result of this study is the Gaussian behavior of a single chain in the system ($U_{AA}{}^{s} = 0$) before the spinodal is reached. In the particular case where the composition is chosen to be 50/50, this is achieved at $|\mathbf{k}| = 0$ and at the critical value of $(\chi_F N)_c = 2$ in the case of binary homopolymer blends A and B and at the values of $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$ and $(\chi_F N)_c \simeq 5.25$ in the case of the diblock copolymer A–B system, where $R_{gA}$ is the radius of gyration of one block chain of species A. These values of $|\mathbf{k}^*|$ and $(\chi_F N)_c$ are identical with those obtained by Leibler using a theoretical approach dealing with the scattering properties.

## I. Introduction

In a previous paper,[1] the screening of interactions in compatible blends of two homopolymers A and B was discussed. In that paper, mean-field and perturbation theory was used to derive general expressions for the effective screening potential $U_{AA}{}^{s}$ and for the radius of gyration $\langle R_{gA}{}^2\rangle$ as a function of the compositions $\Phi_A$ and $\Phi_B$ of both components and their Flory interaction parameter $\chi_F$. The main conclusion of that work was the Gaussian behavior (when the effective screened potential $U_{AA}{}^{s}$ is equal to zero) of one chain within the system before the phase separation (spinodal decomposition) takes place.

In the present paper we mainly discuss the case of diblock copolymer A–B and show that the screening of interactions in such systems provides a similar effect. In this theoretical approach, one treats the fluctuations in the Gaussian approximation. Whereas the Gaussian "point" described above occurs at $|\mathbf{k}| = 0$ for the blend of A and B homopolymers, the total screening or the zero of the effective interaction potential of the A part for the diblock copolymer system at 50/50 composition is obtained at the value of the wave vector $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$, where $R_{gA}$ is the radius of gyration of one block chain of species A. This result is in perfect agreement with the theoretical approach regarding the scattering properties.[2–5]

The present paper is organized as follows: In the next section we calculate first the mean-field Hamiltonian explicitly for the dense melt of diblock copolymers. This Edwards Hamiltonian will provide the generalized random phase approximation (RPA) for diblock copolymer systems. Similar calculations have been attempted in refs 6 and 7. The knowledge of the Edwards Hamiltonian allows us to carry out the screening calculation. This is done in section III of the paper. Hence we integrate out all terms coming from the B parts of the diblock copolymers and we are left with an effective A system in the presence of the mean field coming from the B system. Then the "effective A chains" will screen their effective interaction themselves. Finally, we are left with a single A chain taking into account the presence of all the other A and B species. The final result is therefore the effective Edwards Hamiltonian for one chain, i.e., the configurational part and an effective interaction potential acting on this chain. This effective interaction potential is called the screened potential. In the remainder of the paper we analyze the effective interaction potential and discuss the consequences.

## II. Calculation of the Edwards Hamiltonian for Diblock Copolymers

Let us consider a melt system of a diblock copolymer. First we have to derive the mean-field Edwards Hamil-

---

* To whom correspondence should be addressed.

0024-9297/90/2223-3172$02.50/0

tonian (Edwardsian) for this system. In real space the partition function $Z$ for the block copolymer melt is given by

$$Z([\mathbf{R}_A,\mathbf{R}_B]) = \int \delta\mathbf{R}_A \int \delta\mathbf{R}_B \exp\Big\{-\left(\frac{3}{2l^2}\right)\int_0^{L'}\left(\frac{\partial\mathbf{R}_A}{\partial\mathbf{s}}\right)^2 \mathrm{d}s - \left(\frac{3}{2l^2}\right)\int_{L'}^{L}\left(\frac{\partial\mathbf{R}_B}{\partial\mathbf{s}}\right)^2 \mathrm{d}s - \int_0^{L'}\int_0^{L'} V_{AA}[\mathbf{R}_A(s) - \mathbf{R}_A(s')]\,\mathrm{d}s\,\mathrm{d}s' - \int_{L'}^{L}\int_{L'}^{L} V_{BB}[\mathbf{R}_B(s) - \mathbf{R}_B(s')]\,\mathrm{d}s\,\mathrm{d}s' - \int_0^{L'}\int_{L'}^{L} 2V_{AB}[\mathbf{R}_A(s) - \mathbf{R}_B(s')]\,\mathrm{d}s\,\mathrm{d}s'\Big\} \quad (1)$$

where $\mathbf{R}_A(s)$ and $\mathbf{R}_B(s)$ are all A and B parts of the diblock copolymers, respectively. $V_{\alpha\beta}$ ($\alpha$, $\beta$ = A, B) are the appropriate interaction potentials between the blocks themselves and the different blocks. $s$ is the contour variable and $l$ the effective step length of the copolymer chain, supposed to be equal for both species A and B.

We consider a diblock copolymer A–B where the first part of the contour length $fL$ of the copolymer chain consists of the type A and the second part $(1 - f)L$ of the type B. $f$ is the relative composition of A monomers in the diblock copolymer chain, $0 < f < 1$ (i.e., $L' = fL$; see Figure 1). Instead of having the partition function in the chain variables $\mathbf{R}_A(s)$ and $\mathbf{R}_B(s)$, we want to rewrite $Z$ as a function of the microscopic density variables

$$\rho_{\mathbf{k}}^{A} = \sum_{\substack{\text{all}\\ \text{A monomers}}} \int_0^{fL} \mathrm{d}s\, e^{i\mathbf{k}\mathbf{R}_A(s)} \quad (2)$$

$$\rho_{\mathbf{k}}^{B} = \sum_{\substack{\text{all}\\ \text{B monomers}}} \int_{fL}^{L} \mathrm{d}s\, e^{i\mathbf{k}\mathbf{R}_B(s)} \quad (3)$$

Thus we have to evaluate the following integrals

$$Z([\rho_{\mathbf{k}}^{A},\rho_{\mathbf{k}}^{B}]) = \int \delta\mathbf{R}_A \int \delta\mathbf{R}_B\, Z([\mathbf{R}_A(s),\mathbf{R}_B(s)]) \times \prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^{A} - \int_0^{fL} e^{i\mathbf{k}\mathbf{R}_A(s)}) \prod_{\mathbf{q}} \delta(\rho_{\mathbf{q}}^{B} - \int_{fL}^{L} e^{i\mathbf{q}\mathbf{R}_B(s)}) \quad (4)$$

The transformation of the energetic part of the partition function is straightforward and we will have

$$\exp\{-\int_0^{fL}\int_0^{fL} V_{AA}[\mathbf{R}_A(s) - \mathbf{R}_A(s')]\,\mathrm{d}s\,\mathrm{d}s'\} \times \exp\{-\int_{fL}^{L}\int_{fL}^{L} V_{BB}[\mathbf{R}_B(s) - \mathbf{R}_B(s')]\,\mathrm{d}s\,\mathrm{d}s'\} \times \exp\{-\int_0^{fL}\int_{fL}^{L} 2V_{AB}[\mathbf{R}_A(s) - \mathbf{R}_B(s')]\,\mathrm{d}s\,\mathrm{d}s'\} = \exp\{-V_{AA}\sum_{\mathbf{k}} \rho_{\mathbf{k}}^{A}\rho_{-\mathbf{k}}^{A} - V_{BB}\sum_{\mathbf{k}} \rho_{\mathbf{k}}^{B}\rho_{-\mathbf{k}}^{B} - 2V_{AB}\sum_{\mathbf{k}} \rho_{\mathbf{k}}^{A}\rho_{-\mathbf{k}}^{B}\} \quad (5)$$

This is valid under the assumption that the potentials $V_{\alpha\beta}$ are short ranged, i.e.

$$V_{\alpha\beta}(\mathbf{R} - \mathbf{R}') = V_{\alpha\beta}\delta(\mathbf{R} - \mathbf{R}') \quad (6)$$

Therefore we are left with the Jacobian

$$J = \int \delta\mathbf{R}_A(s)\delta\mathbf{R}_B(s) \exp\Big\{-\left(\frac{3}{2l^2}\right)\int_0^{fL} \mathbf{R}_A'^2(s)\,\mathrm{d}s - \left(\frac{3}{2l^2}\right)\int_{fL}^{L} \mathbf{R}_B'^2(s)\,\mathrm{d}s\Big\} \prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^{A} - \int_0^{fL} e^{i\mathbf{k}\mathbf{R}_A(s)}) \prod_{\mathbf{q}} \delta(\rho_{\mathbf{q}}^{B} - \int_{fL}^{L} e^{i\mathbf{k}\mathbf{R}_B(s)}) \quad (7)$$

where we have assumed that the $\sum_{\text{all monomers}}$ is absorbed into the $\int$ sign and $\mathbf{R}' = (\partial\mathbf{R}/\partial\mathbf{s})$. To proceed further it

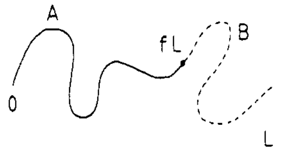

**Figure 1.** See text.

is useful to parameterize the $\delta$ function as

$$\prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^{A} - \int_0^{fL} \exp\{i\mathbf{k}\mathbf{R}_A(s)\}\,\mathrm{d}s) = \int \delta\phi_{\mathbf{k}} \exp\{i\sum_{\mathbf{k}} \phi_{\mathbf{k}}(\rho_{-\mathbf{k}} - \int_0^{fL} e^{i\mathbf{k}\mathbf{R}_A(s)}\,\mathrm{d}s)\} \quad (8a)$$

$$\prod_{\mathbf{q}} \delta(\rho_{\mathbf{q}}^{B} - \int_{fL}^{L} \exp\{i\mathbf{q}\mathbf{R}_B(s)\}\,\mathrm{d}s) = \int \delta\psi_{\mathbf{q}} \exp\{i\sum_{\mathbf{q}} \psi_{\mathbf{q}}(\rho_{-\mathbf{q}} - \int_{fL}^{L} e^{i\mathbf{q}\mathbf{R}_B(s)}\,\mathrm{d}s)\} \quad (8b)$$

where $\delta\phi_{\mathbf{k}}$ and $\delta\psi_{\mathbf{q}}$ are functional integrals over the set of functions $\phi_{\mathbf{k}}$ and $\psi_{\mathbf{q}}$. Thus we find for the Jacobian the following expression:

$$J = \int \prod_{\mathbf{k}} \delta\phi_{\mathbf{k}} \prod_{\mathbf{q}} \delta\psi_{\mathbf{q}} \exp\{i\sum_{\mathbf{q}} \psi_{\mathbf{q}}\rho_{-\mathbf{q}}^{B}\} \exp\{i\sum_{\mathbf{k}} \phi_{\mathbf{k}}\rho_{-\mathbf{k}}^{A}\} \times \int \delta\mathbf{R}_A\delta\mathbf{R}_B \exp\Big\{-\left(\frac{3}{2l^2}\right)\int \mathbf{R}_A'^2(s)\,\mathrm{d}s - \left(\frac{3}{2l^2}\right)\int \mathbf{R}_B'^2(s)\,\mathrm{d}s\Big\}\Big\{1 - i\sum_{\mathbf{k}} \phi_{\mathbf{k}} \int_0^{fL} \mathrm{d}s\, e^{i\mathbf{k}\mathbf{R}_A(s)} - \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} \phi_{\mathbf{k}}\phi_{\mathbf{k}'} \int_0^{fL}\int_0^{fL} \mathrm{d}s\,\mathrm{d}s'\, e^{i\mathbf{k}\mathbf{R}_A(s)+i\mathbf{k}'\mathbf{R}_A(s')}\Big\}\Big\{1 - i\sum_{\mathbf{q}} \psi_{\mathbf{q}} \int_{fL}^{L} \mathrm{d}s\, e^{i\mathbf{q}\mathbf{R}_B(s)} - \frac{1}{2}\sum_{\mathbf{q},\mathbf{q}'} \psi_{\mathbf{q}}\psi_{\mathbf{q}'} \int_{fL}^{L}\int_{fL}^{L} \mathrm{d}s\,\mathrm{d}s'\, e^{i\mathbf{q}\mathbf{R}_B(s)+i\mathbf{q}'\mathbf{R}_B(s')}\Big\} \quad (9)$$

where we have expanded out the exponential to orders $\phi^2$ and $\psi^2$ and higher orders in the auxilliary fields are neglected. By multiplying the last two brackets in eq 9 we find a cross term

$$\phi_{\mathbf{k}}\psi_{\mathbf{q}} \int_0^{fL} e^{i\mathbf{k}\mathbf{R}_A(s)}\,\mathrm{d}s \int_{fL}^{L} e^{i\mathbf{q}\mathbf{R}_B(s)}\,\mathrm{d}s \quad (10)$$

which is of second order also. The integrals over the chain variables $\mathbf{R}_A(s)$ and $\mathbf{R}_B(s)$ can now be carried out, and we find with the definitions of the "bare" structure factors $S_{\alpha\beta}^{0}(\mathbf{k})$

$$S_{\alpha\beta}^{0}(\mathbf{k}) = \int\int \langle e^{i\mathbf{k}(\mathbf{R}_\alpha(s)-\mathbf{R}_\beta(s'))}\rangle_0\,\mathrm{d}s\,\mathrm{d}s' \quad (11a)$$

where $\langle\ \rangle_0$ is the unperturbed average over the Wiener measure

$$\exp[-\int \mathbf{R}_A'^2(s)\,\mathrm{d}s - \int \mathbf{R}_B'^2(s)\,\mathrm{d}s] \quad (11b)$$

Hence in terms of $S_{\alpha\beta}^{0}(\mathbf{k})$ the Jacobian is written as

$$J = \int \prod_{\mathbf{k}} \delta\phi_{\mathbf{k}} \int \prod_{\mathbf{k}} \delta\psi_{\mathbf{k}} \exp\{i\sum_{\mathbf{k}} \phi_{\mathbf{k}}\rho_{-\mathbf{k}}^{A} + i\sum_{\mathbf{k}} \psi_{\mathbf{k}}\rho_{-\mathbf{k}}^{B}\} \exp\Big\{-\frac{1}{2}\sum_{\mathbf{k}} |\phi_{\mathbf{k}}|^2 S_{AA}^{0}(\mathbf{k}) - \frac{1}{2}\sum_{\mathbf{k}} |\psi_{\mathbf{k}}|^2 S_{BB}^{0}(\mathbf{k}) - \sum_{\mathbf{k}} \psi_{\mathbf{k}}\phi_{-\mathbf{k}} S_{AB}^{0}(\mathbf{k})\Big\} \quad (12)$$

Note that we have reexponentiated the expansion as follows:

$$1 - \frac{1}{2}\phi^2 S_{\mathrm{AA}}^{0}(\mathbf{k}) - \frac{1}{2}\psi^2 S_{\mathrm{BB}}^{0}(\mathbf{k}) - \phi\psi S_{\mathrm{AB}}^{0}(\mathbf{k}) \simeq \exp\left\{-\frac{1}{2}\phi^2 S_{\mathrm{AA}}^{0}(\mathbf{k}) - \frac{1}{2}\psi^2 S_{\mathrm{BB}}^{0}(\mathbf{k}) - \phi\psi S_{\mathrm{AB}}^{0}(\mathbf{k})\right\} \quad (13)$$

The $\phi$ and $\psi$ integrations are simple Gaussian integrals and can be done at once so that we finally quote the result for the Jacobian:

$$J = \exp\left\{-\sum_{\mathbf{k}} \frac{1}{\Delta S^0(\mathbf{k})}[\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{A}} S_{\mathrm{BB}}^{0}(\mathbf{k}) + \rho_{\mathbf{k}}^{\mathrm{B}}\rho_{-\mathbf{k}}^{\mathrm{B}} S_{\mathrm{AA}}^{0}(\mathbf{k}) - 2\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{B}} S_{\mathrm{AB}}^{0}(\mathbf{k})]\right\} \quad (14)$$

where

$$\Delta S^0(\mathbf{k}) = S_{\mathrm{AA}}^{0}(\mathbf{k}) S_{\mathrm{BB}}^{0}(\mathbf{k}) - S_{\mathrm{AB}}^{02}(\mathbf{k}) \quad (15)$$

Taking into account the interactions $V_{\alpha\beta}$ ($\alpha$, $\beta$ = A, B), we write the mean-field Edwardsian for the block copolymers as

$$H = \sum_{\mathbf{k}}\left\{\left(\frac{1}{\Delta S^0(\mathbf{k})} S_{\mathrm{BB}}^{0}(\mathbf{k}) + V_{\mathrm{AA}}\right)\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{A}} + \left(\frac{1}{\Delta S^0(\mathbf{k})} S_{\mathrm{AA}}^{0}(\mathbf{k}) + V_{\mathrm{BB}}\right)\rho_{\mathbf{k}}^{\mathrm{B}}\rho_{-\mathbf{k}}^{\mathrm{B}} - 2\left(\frac{1}{\Delta S^0(\mathbf{k})} S_{\mathrm{AB}}^{0}(\mathbf{k}) - V_{\mathrm{AB}}\right)\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{B}}\right\} \quad (16)$$

If the system is incompressible, i.e.

$$\rho_{\mathbf{k}}^{\mathrm{A}} + \rho_{\mathbf{k}}^{\mathrm{B}} = 0 \qquad \forall\, \mathbf{k} > 0 \quad (17\mathrm{a})$$

and

$$\rho_0^{\mathrm{A}} + \rho_0^{\mathrm{B}} = \bar{\rho}_0 \qquad \text{for } \mathbf{k} = 0 \quad (17\mathrm{b})$$

we finally find

$$H = \sum_{\mathbf{k}}\left(\frac{S_{\mathrm{T}}^{0}(\mathbf{k})}{\Delta S^0(\mathbf{k})} - 2\chi_{\mathrm{F}}\right)\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{A}} \quad (18)$$

where

$$2\chi_{\mathrm{F}} = 2V_{\mathrm{AB}} - (V_{\mathrm{AA}} + V_{\mathrm{BB}}) \quad (19)$$

$$S_{\mathrm{T}}^{0}(\mathbf{k}) = S_{\mathrm{AA}}^{0}(\mathbf{k}) + S_{\mathrm{BB}}^{0}(\mathbf{k}) + 2S_{\mathrm{AB}}^{0}(\mathbf{k}) \quad (20)$$

This result is valid for any diblock copolymer. Note that relation 18 resembles the classical random phase approximation (RPA) result for diblock copolymers.[2] For $S_{\mathrm{AB}}^{0}(\mathbf{k}) = 0$, i.e., an ordinary AB blend, it reduces to

$$H = \sum_{\mathbf{k}}\left(\frac{1}{S_{\mathrm{AA}}^{0}(\mathbf{k})} + \frac{1}{S_{\mathrm{BB}}^{0}(\mathbf{k})} - 2\chi_{\mathrm{F}}\right)\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{A}} \quad (21)$$

which is identical with de Gennes' celebrated equation.[8]

## III. Calculation of the Effective Screened Potential $U_{\mathrm{AA}}^{\mathrm{s}}$

The effective partition function $Z_{\mathrm{A}}$ for all blocks of type A, taking into account the presence of all blocks of type B, is obtained by integrating out the variables containing the B blocks to get

$$Z_{\mathrm{A}} = \int \prod_{\mathbf{k}} \mathrm{d}\rho_{\mathbf{k}}^{\mathrm{A}}\, \mathrm{d}\rho_{-\mathbf{k}}^{\mathrm{A}} \exp\{-H_{\mathrm{AA}}\} \quad (22)$$

where $H_{\mathrm{AA}}$ is the Edwards Hamiltonian of the effective A system, which is given by

$$H_{\mathrm{AA}} = \sum_{\mathbf{k}}\left\{\frac{S_{\mathrm{BB}}^{0}(\mathbf{k})}{\Delta S^0(\mathbf{k})} + V_{\mathrm{AA}} - \frac{\left(\dfrac{S_{\mathrm{AB}}^{0}(\mathbf{k})}{\Delta S^0(\mathbf{k})} - V_{\mathrm{AB}}\right)^2}{\dfrac{S_{\mathrm{AA}}^{0}(\mathbf{k})}{\Delta S^0(\mathbf{k})} + V_{\mathrm{BB}}}\right\}\rho_{\mathbf{k}}^{\mathrm{A}}\rho_{-\mathbf{k}}^{\mathrm{A}} \quad (23)$$

This is the final effective Hamiltonian of all species A present in the system. The first term is the configurational part, whereas the second and the third terms represent the screened potential. Now we have to integrate out all effective A blocks ("dressed" with the interactions coming from the B part of the copolymer) to obtain the final screened potential of one representative A block. This is equivalent to the screening of the effective potential[9] calculated in eq 23. The effective Hamiltonian for one block of type A is given by

$$Z_{\mathrm{A}} = \int \mathrm{D}\mathbf{R}(s) \exp\left\{-\frac{3}{2l^2}\int_0^{N_{\mathrm{A}}} \mathrm{d}s\, \mathbf{R}_{\mathrm{A}}'^2(s) - \int_0^{N_{\mathrm{A}}}\mathrm{d}s \int_0^{N_{\mathrm{A}}} \mathrm{d}s'\, U^{\mathrm{s}}_{\mathrm{AA,C}}[\mathbf{R}(s) - \mathbf{R}(s')]\right\} \quad (24)$$

where

$$U^{\mathrm{s}}_{\mathrm{AA,C}} = \left\{V_{\mathrm{AA}} + \Delta V S_{\mathrm{BB}}^{0}(\mathbf{k}) - \frac{[S_{\mathrm{AB}}^{0}(\mathbf{k})]^2}{S_{\mathrm{AA}}^{0}(\mathbf{k})}\left(\Delta V - \frac{V_{\mathrm{BB}}}{S_{\mathrm{AA}}^{0}(\mathbf{k})} - 2\frac{V_{\mathrm{AB}}}{S_{\mathrm{AB}}^{0}(\mathbf{k})}\right)\right\}\Bigg/\{1 + V_{\mathrm{AA}}S_{\mathrm{AA}}^{0}(\mathbf{k}) + V_{\mathrm{BB}}S_{\mathrm{BB}}^{0}(\mathbf{k}) + 2V_{\mathrm{AB}}S_{\mathrm{AB}}^{0}(\mathbf{k}) + \Delta V \Delta S^0(\mathbf{k})\} \quad (25)$$

and

$$\Delta V = V_{\mathrm{AA}}V_{\mathrm{BB}} - V_{\mathrm{AB}}^{2} \quad (26)$$

We present an alternative "heuristic" derivation of the screened potential in the Appendix. $U^{\mathrm{s}}_{\mathrm{AA,C}}$ is the effective mean-field potential of one block of species A taking into account the presence of all the other blocks of species A and B. One notes that the expression of the effective screening potential in the case of the blend of two homopolymers A and B can be deduced from the above equation by setting $S_{\mathrm{AB}}^{0}(\mathbf{k}) = 0$ (see relation 6 in ref 1)

$$U^{\mathrm{s}}_{\mathrm{AA,H}} = \frac{V_{\mathrm{AA}} + \Delta V S_{\mathrm{BB}}^{0}(\mathbf{k})}{1 + V_{\mathrm{AA}}S_{\mathrm{AA}}^{0}(\mathbf{k}) + V_{\mathrm{BB}}S_{\mathrm{BB}}^{0}(\mathbf{k}) + \Delta V S_{\mathrm{AA}}^{0}(\mathbf{k}) S_{\mathrm{BB}}^{0}(\mathbf{k})} \quad (27)$$

The subscripts "C" and "H" refer to copolymer and homopolymer system, respectively. Before we go on to the discussion of the effective potential $U^{\mathrm{s}}_{\mathrm{AA}}$ in both cases (copolymer A–B and the mixture A and B), a few remarks can be made on some interesting limits.

(i) If one considers the special case where $V_{\mathrm{AA}} = V_{\mathrm{BB}} = V_{\mathrm{AB}} = V$ (i.e., *noninteracting system* $\chi_{\mathrm{F}} = 0$), $U^{\mathrm{s}}_{\mathrm{AA}}$ reduces to

(*a*) *Copolymer System A–B*

$$U^{\mathrm{s}}_{\mathrm{AA,C}} = \frac{V\left[1 + \dfrac{[S_{\mathrm{AB}}^{0}(\mathbf{k})]^2}{S_{\mathrm{AA}}^{0}(\mathbf{k})}\left(\dfrac{1}{S_{\mathrm{AA}}^{0}(\mathbf{k})} + \dfrac{2}{S_{\mathrm{AB}}^{0}(\mathbf{k})}\right)\right]}{1 + V[S_{\mathrm{AA}}^{0}(\mathbf{k}) + S_{\mathrm{BB}}^{0}(\mathbf{k}) + 2S_{\mathrm{AB}}^{0}(\mathbf{k})]} \quad (28)$$

*(b) Blend of Homopolymers A and B* ($S_{AA}{}^0 = 0$)

$$U^s{}_{AA,H} = \frac{V}{1 + V[S_{AA}{}^0(\mathbf{k}) + S_{BB}{}^0(\mathbf{k})]} \tag{29}$$

In the latter case we recover the screened potential derived by Edwards.[10]

*(ii) Interacting Systems* ($\chi_F \neq 0$). This can be achieved by choosing $V_{AA} = V_{BB} = V$ and $V_{AB} = V + \chi_F$. In this case $U^s{}_{AA}$ is given by

*(a) Copolymer Systems A–B*

$$U^s{}_{AA,C} = \left[ V\left\{1 + \frac{S_{AB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\left(2 + \frac{S_{AB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\right) - 2\chi_F\frac{\Delta S^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\right\} + 2\chi_F\frac{S_{AB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\right] \Big/ [1 + V[S_T{}^0(\mathbf{k}) - 2\chi_F\Delta S^0(\mathbf{k})] + 2\chi_F S_{AB}{}^0(\mathbf{k})] \tag{30}$$

When $V \to \infty$, the limit exists and eq 30 reduces to

$$\lim_{V\to\infty} U^s{}_{AA,C} = \frac{1 + \dfrac{S_{AB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\left(2 + \dfrac{S_{AB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}\right) - 2\chi_F\dfrac{\Delta S^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k})}}{S_T{}^0(\mathbf{k}) - 2\chi_F\Delta S^0(\mathbf{k})} \tag{31}$$

which corresponds to the case of the melt interacting copolymer system limit.

*(b) Blend of Homopolymer A and B* ($S_{AB}{}^0 = 0$)

$$U^s{}_{AA,H} = \frac{V[1 - 2\chi_F S_{BB}{}^0(\mathbf{k})]}{1 + V[S_{AA}{}^0(\mathbf{k}) + S_{BB}{}^0(\mathbf{k}) - 2\chi_F S_{AA}{}^0(\mathbf{k})S_{BB}{}^0(\mathbf{k})]} \tag{32}$$

When $V \to \infty$, the limit exists and relation 32 reduces to

$$\lim_{V\to\infty} U^s{}_{AA,H} = \frac{1 - 2\chi_F S_{BB}{}^0(\mathbf{k})}{S_{AA}{}^0(\mathbf{k}) + S_{BB}{}^0(\mathbf{k}) - 2\chi_F S_{AA}{}^0(\mathbf{k})S_{BB}{}^0(\mathbf{k})} \tag{33}$$

which is the expression of the effective screened potential in the melt state and is identical with relation 7 in the previous paper.[1] In these theoretical results, it has been assumed that $\chi/V$ is small compared to unity.

## IV. Discussion of the Effective Screened Potential $U^s{}_{AA}$

**(a) Blend of Homopolymers A and B ($S_{AB}{}^0 = 0$).** For the sake of simplicity let us assume that the homopolymers have the same molecular weight or the same degree of polymerization (i.e., $N_A = N_B = N$) and the same radius of gyration $R_{gA} = R_{gB}$ [i.e., $P_A(\mathbf{k}) = P_B(\mathbf{k}) = P(\mathbf{k})$]; $P(\mathbf{k})$ is the intramolecular form factor. In this case the "bare" structure factors $S_{ij}{}^0(\mathbf{k})$ are given by

$$S_{AA}{}^0(\mathbf{k}) = \Phi_A N P(\mathbf{k}) \tag{34}$$

$$S_{BB}{}^0(\mathbf{k}) = (1 - \Phi_A) N P(\mathbf{k}) \tag{35}$$

where $\Phi_A$ is the composition of species A in the mixture A and B, and $P(\mathbf{k})$ is the Debye function (for Gaussian chains). Substituting the expressions of $S_{ij}{}^0(\mathbf{k})$ in relation 33, one obtains

$$U^s{}_{AA,H} = \frac{1}{NP(\mathbf{k})}\left(\frac{1 - 2\chi_F N(1 - \Phi_A)P(\mathbf{k})}{1 - 2\chi_F N\Phi_A(1 - \Phi_A)P(\mathbf{k})}\right) \tag{36}$$

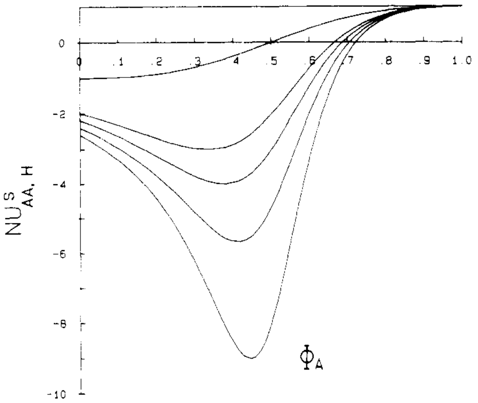

**Figure 2.** Variation of the effective screened potential $NU^s{}_{AA,H}$ as a function of the composition $\Phi_A$ in the case of a mixture of two homopolymers A and B for different values of $\chi_F N$. From top to bottom, $\chi_F N$ = 0, 1, 1.5, 1.6, 1.7, and 1.8.

Introducing $\chi_c(\mathbf{k})$ as the critical interaction parameter

$$\chi_c(\mathbf{k}) = \{2\Phi_A(1 - \Phi_A)NP(\mathbf{k})\}^{-1} \tag{37}$$

We can rewrite $U^s{}_{AA,H}$ as

$$U^s{}_{AA,H} = \frac{1}{NP(\mathbf{k})}\left(\frac{1 - 2\chi_F N(1 - \Phi_A)P(\mathbf{k})}{1 - \chi_F/\chi_c(\mathbf{k})}\right) \tag{38}$$

This relation shows that the effective screened potential changes sign when

$$\chi_F = \frac{1}{2N(1 - \Phi_A)P(\mathbf{k})} \tag{39}$$

and diverges at

$$\chi_F = \chi_c(\mathbf{k}) = \{2\Phi_A(1 - \Phi_A)NP(\mathbf{k})\}^{-1} \tag{40}$$

To illustrate this behavior we have plotted in Figure 2 the variation of the effective screened potential $U^s{}_{AA,H}$ at $|\mathbf{k}| = 0$ [$P(\mathbf{k} = 0) = 1$] as a function of composition $\Phi_A$ for different values of $\chi_F N$, namely, 0, 1, 1.5, 1.6, 1.7, and 1.8. From this representation some remarks can be made:

(*i*) *Small $\Phi_A$ Range.* In this range of composition when the quantity $\chi_F N$ increases, i.e., if the molecular weight is high enough and/or if the system is slightly incompatible, the effective screened potential changes sign and becomes negative (attractive) before the phase separation is reached for $\chi_F N = 2$ at 50/50 composition.

(*ii*) *High $\Phi_A$ Range.* The effective screened potential is always positive (repulsive). This is probably due to the high quantity of species A present within the mixture. In this case and because of the symmetry of the system, the Gaussian behavior is shifted to the B species.

**(b) Diblock Copolymer A–B System.** In order to illustrate the main points of our analysis we consider the special case of diblock copolymers of two components A and B with $N_A$ and $N_B$ monomers. The "bare" structure factors $S_{ij}{}^0(\mathbf{k})$ are given by[2]

$$S_{AA}{}^0(\mathbf{k}) = (N_A + N_B)P_A(f,\mathbf{k}) \tag{41}$$

$$S_{BB}{}^0(\mathbf{k}) = (N_A + N_B)P_B(1-f,\mathbf{k}) \tag{42}$$

$$S_{AB}{}^0(\mathbf{k}) = S_{BA}{}^0(\mathbf{k}) = (N_A + N_B)P_{AB}(f,\mathbf{k}) \tag{43}$$

where $P_A(f,\mathbf{k})$, $P_B(1-f,\mathbf{k})$, and $P_{AB}(f,\mathbf{k})$ are the intramolecular form factors for blocks A and B and the intramolecular interference form factor between blocks A and B, respectively. For an ideal copolymer chain these form

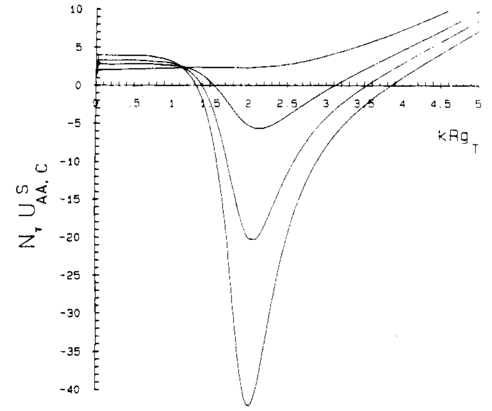

**Figure 3.** Variation of the effective screened potential $N_T U^s_{AA,C}$ as a function of $\mathbf{k}R_{gT}$ in the case of diblock copolymer at $\chi_F N_T = 10$ and for different values of composition $f$. From bottom to top, $f = 0.5$, 0.55, 0.6, and 0.7.

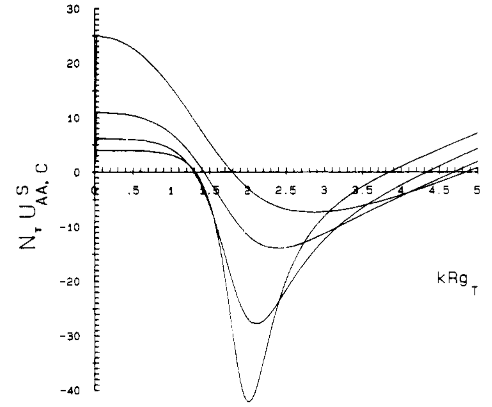

**Figure 4.** Same as Figure 3 for different values of $f$. From bottom to top, $f = 0.5$, 0.4, 0.3, and 0.2.

factors are represented by the modified Debye function, namely

$$P_A(f,\mathbf{k}) = 2(e^{-fu} + fu - 1)/u^2 \qquad (44)$$

$$P_B(1-f,\mathbf{k}) = 2(e^{-(1-f)u} + (1-f)u - 1)/u^2 \qquad (45)$$

$$P_{AB}(f,\mathbf{k}) = [P_A(1,\mathbf{k}) - P_A(f,\mathbf{k}) - P_B(1-f,\mathbf{k})]/2 \qquad (46)$$

where $u = \mathbf{k}^2 R_{gT}^2$ and $R_{gT}$ is the radius of gyration of diblock copolymer chain. Substituting relations 41–46 into eq 31, one obtains finally for the effective screened potential the following expression:

$$N_T U^s_{AA,C} = \left\{1 + \frac{P_{AB}(f,\mathbf{k})}{P_A(f,\mathbf{k})}\left(2 + \frac{P_{AB}(f,\mathbf{k})}{P_A(f,\mathbf{k})}\right) - 2\chi_F N_T\left(P_B(1-f,\mathbf{k}) - \frac{P_{AB}^2(f,\mathbf{k})}{P_A(f,\mathbf{k})}\right)\right\}\Big/\{P_A(1,\mathbf{k}) - 2\chi_F N_T[P_A(f,\mathbf{k})P_B(1-f,\mathbf{k}) - P_{AB}^2(f,\mathbf{k})]\} \qquad (47)$$

where $N_T = N_A + N_B$. Figures 3 and 4 show the effect of composition $f$ on the variation of the screened potential with $|\mathbf{k}|R_{gT}$ at $\chi_F N_T = 10$. One observes that the maximum of $|U^s_{AA,C}|$ is obtained for the value of $f = 0.5$, which corresponds to the symmetric diblock copolymer, and $|U^s_{AA,c}|$ diverges at the critical value of $(\chi_F N_T)_c = 10.5$. On the other hand, the position of the peak (maximum of $|U^s_{AA,C}|$) is reached at the value of $|\mathbf{k}|^* R_{gT} \simeq 2$. These values of $|\mathbf{k}|^*$ and $(\chi_F N_T)_c$ are identical with those obtained by Leibler.[2] For values of $f$ different from 0.5, this peak becomes less and less pronounced and disappears completely for other values of $f$ as shown in Figures 3 and 4. The effective screened potential acting on block B, i.e., $U^s_{BB,C}$, can be deduced from relation 31 by just interchanging $S_{AA}^0(\mathbf{k})$ by $S_{BB}^0(\mathbf{k})$:

$$U^s_{BB,C} = \frac{1 + \dfrac{S_{AB}^0(\mathbf{k})}{S_{BB}^0(\mathbf{k})}\left(2 + \dfrac{S_{AB}^0(\mathbf{k})}{S_{BB}^0(\mathbf{k})}\right) - 2\chi_F\dfrac{\Delta S^0(\mathbf{k})}{S_{BB}^0(\mathbf{k})}}{S_T^0(\mathbf{k}) - 2\chi_F \Delta S^0(\mathbf{k})} \qquad (48)$$

Inserting relations 41–46 into relation 48, one obtains for the screened potential acting on block B the following relation:

$$N_T U^s_{BB,C} = \left\{1 + \frac{P_{AB}(f,\mathbf{k})}{P_B(1-f,\mathbf{k})}\left(2 + \frac{P_{AB}(f,\mathbf{k})}{P_B(1-f,\mathbf{k})}\right) - 2\chi_F N_T\left(P_A(f,\mathbf{k}) - \frac{P_{AB}^2(f,\mathbf{k})}{P_B(1-f,\mathbf{k})}\right)\right\}\Big/\{P_A(1,\mathbf{k}) - 2\chi_F N_T[P_A(f,\mathbf{k})P_B(1-f,\mathbf{k}) - P_{AB}^2(f,\mathbf{k})]\} \qquad (49)$$

Since $U^s_{BB,C}$ can be deduced from $U^s_{AA,C}$ by replacing $f$ by $(1 - f)$, it is clear that the variation of $U^s_{BB,C}$ with $|\mathbf{k}|R_{gT}$ as a function of $f$ is identical with the variation of $U^s_{AA,C}$ as a function of $(1 - f)$ (see Figures 3 and 4).

From the previous discussion it is obvious that the 50/50 diblock copolymer system is more interesting. Indeed, the maximum of the effective screened potential, $|U^s_{AA,C}|_{max}$, is reached for the value of $f = 0.5$, and the position peak is well defined. Moreover, in this case the relations are simple and a comparison between the diblock copolymer system (50/50) and the blend of two homopolymers A and B having the same molecular weight could be easily done.

Under these considerations, the "bare" structure factors in the case of the diblock copolymer system are given by[2,4,5]

$$S_{AA}^0(\mathbf{k}) = (N/2)P_{1/2}(\mathbf{k}) \qquad (50)$$

$$S_{BB}^0(\mathbf{k}) = (N/2)P_{1/2}(\mathbf{k}) \qquad (51)$$

$$S_{AB}^0(\mathbf{k}) = S_{BA}^0(\mathbf{k}) = (N/2)P_{AB}(\mathbf{k}) \qquad (52)$$

where

$$P_{AB}(\mathbf{k}) = P_T(\mathbf{k}) - 2P_{1/2}(\mathbf{k}) \qquad (53)$$

In these relations $N = N_A = N_B = N_T/2$, and $P_{1/2}(\mathbf{k})$ is the form factor of species A or B in the diblock 50/50 copolymer chain. $P_T(\mathbf{k}) = P(1,\mathbf{k})$ is the total form factor for the diblock copolymer chain. These form factors are normalized to unity for $|\mathbf{k}| = 0$. Substituting relations 50–53 into eq 31, one obtains finally for the effective screened potential the following expression:

$$U^s_{AA,C} = \frac{\dfrac{P(\mathbf{k})}{P_{1/2}^2(\mathbf{k})} - \chi_F N\left\{1 - \dfrac{P_T(\mathbf{k})}{P_{1/2}(\mathbf{k})}\right\}}{\left(\dfrac{N}{2}\right)\{1 - \chi_F N(P_{1/2}(\mathbf{k}) - P_T(\mathbf{k}))\}} \qquad (54)$$

Since from eqs 38 and 54 it turns out that the effective screened potential is strongly $\mathbf{k}$ dependent, the next section will be consecrated to the variation of $U^s_{AA}$ as a function of $\mathbf{k}$ for different values of $\chi_F N$.

## V. Wave Vector Dependence of the Effective Screened Potential $U^s_{AA}$ at 50/50 Composition

In this section we compare the spatial dependence of the screened potential $U^s_{AA}$ in the case of copolymer and homopolymer systems at 50/50 composition. In order to do this, let us recall the **k** dependence of $U^s_{AA}$ in both cases which is valid for any composition.

*(a) Blend of Homopolymers A and B* ($S_{AB}^0 = 0$)

$$NU^s_{AA,H} = \frac{1 - 2\chi_F N(1-\Phi_A)P(\mathbf{k})}{1-\chi_F/\chi_c(\mathbf{k})} \tag{55}$$

where

$$\chi_c(\mathbf{k}) = \{2N\varphi_A(1-\Phi_A)P(\mathbf{k})\}^{-1} \tag{56}$$

and for $\Phi_A = \Phi_B = 1/2$, the effective screened potential reduces to

$$NU^s_{AA,H} = \frac{1-\chi_F NP(\mathbf{k})}{1-\frac{\chi_F N}{2}P(\mathbf{k})} \tag{57}$$

*(b) 50/50 Diblock Copolymer (A-B)*

This case is merely a junction of two homopolymers A and B at 50/50 composition and

$$U^s_{AA,C} = \frac{2\left[\frac{P_T(\mathbf{k})}{P_{1/2}^2(\mathbf{k})} - \chi_F N\left(1-\frac{P_T(\mathbf{k})}{P_{1/2}(\mathbf{k})}\right)\right]}{1-\chi_F N[P_{1/2}(\mathbf{k})-P_T(\mathbf{k})]} \tag{58}$$

In the case of a mixture of two homopolymers A and B (50/50 composition), as one can see from eq 52, before the spinodal is reached (phase separation; $|U^s_{AA}| \rightarrow \infty$), the effective screened potential goes to zero for $\chi_F N = 1$, which corresponds to a Gaussian behavior, then it becomes negative for $1 < \chi_F N < 2$, and finally it diverges at $\chi_F N = 2$. This is true at the value of $|\mathbf{k}| = 0$.

As far as the case of diblock copolymer is concerned, the situation is more subtle. Indeed, from eq 53, one can see that before the spinodal decomposition or the microphase separation takes place ($U^s_{AA,C} \rightarrow \infty$), $U^s_{AA,C}$ goes to zero for

$$1 = \chi_F N\frac{P_{1/2}(\mathbf{k})}{P_T(\mathbf{k})}[P_{1/2}(\mathbf{k})-P_T(\mathbf{k})] \tag{59}$$

*Contrary to the mixture of homopolymers A and B, this can never be the case for* $\mathbf{k} = 0$ *since by definition the quantities* $P_{1/2}(\mathbf{k}=0)$ *and* $P_T(\mathbf{k}=0)$ *are equal to unity.* Therefore the variation with the wave vector **k** has to be considered. Since it is obvious from the preceding discussion that $U^s_{AA}$ is strongly **k** dependent, it was interesting to plot this quantity as a function of $\mathbf{k}R_{gA}$. This has been done in Figures 5 and 6, where we have plotted, in arbitrary units, $NU^s_{AA,H}$ and $NU^s_{AA,C}$ for different values of $\chi_F N$ in the case of blend A/B (50/50) and copolymer A-B (50/50), respectively.

In the case of binary blends of two homopolymers at 50/50 composition, it can be seen from Figure 5 that, at the value of $|\mathbf{k}| = 0$, the effective screened potential $U^s_{AA,H}$ changes sign at the value of $(\chi_F N)_0 = 1$ until its divergence, which occurs at $(\chi_F N)_c = 2$. In other words, the chain behaves Gaussian ($U^s_{AA,H} = 0$), and then it shrinks until the phase separation or the spinodal decomposition is reached ($|U^s_{AA,H} \rightarrow \infty$).

As regards the diblock copolymer system, which is illustrated in Figure 6, the same situation is observed but shifted at the value of $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$. Indeed when $\chi_F N$ increases (for instance if the molecular weight of the copolymer is too large or if the system is slightly incompatible), $U^s_{AA,C}$ vanishes at $(\chi_F N)_0 \simeq 3.4$ and then becomes negative (attractive) for the values of $\chi_F N > (\chi_F N)_0$ until it reaches microphase separation, which occurs at $(\chi_F N)_c \simeq 5.25$. The two species become incompatible and form microdomains with lamellar structures.[2] These values of $|\mathbf{k}^*|$ and $(\chi_F N)_c$, namely, $2^{1/2}/R_{gA}$ and 5.25, respectively, are identical with those calculated by Leibler.[2]

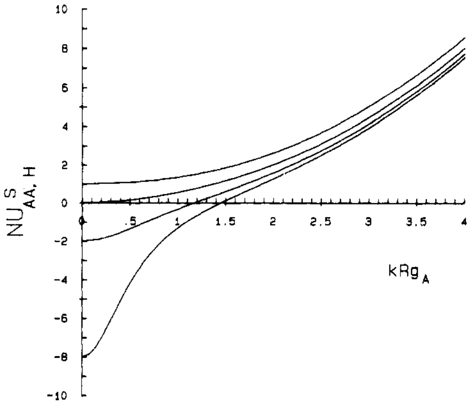

**Figure 5.** Variation of the effective screened potential $NU^s_{AA,H}$ as a function of $\mathbf{k}R_{gA}$ in the case of a mixture of two homopolymers A and B (at the same composition $\Phi_A = \Phi_B = 1/2$) at different values of $\chi_F N$. From top to bottom, $\chi_F N = 0, 1, 1.5$, and 1.8 ($|NU^s_{AA,H}| \rightarrow \infty$ at $(\chi_F N)_c = 2$).

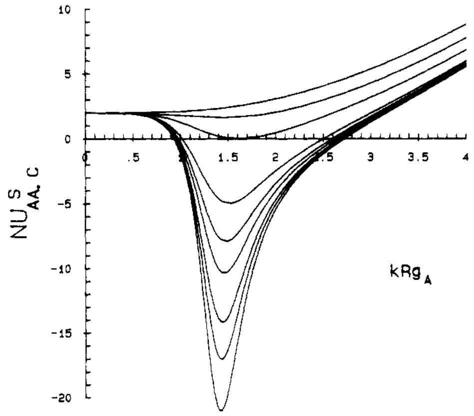

**Figure 6.** Variation of the effective screened potential $NU^s_{AA,C}$ as a function of $\mathbf{k}R_{gA}$ in the case of diblock copolymer 50/50 at different values of $\chi_F N$. From top to bottom, $\chi_F N = 0$ to 5; $|NU^s_{AA,C}| = 0$ at $\chi_F N \simeq 3.4$.

## VI. Conclusion

In this paper, we have discussed the screening of interactions in compatible binary homopolymer blends A and B and in diblock copolymer A-B systems. The theoretical variation of the effective screened potential $U^s_{AA}$ as a function of the composition is studied in the case of homopolymer blends A and B. The **k** dependence of $U^s_{AA}$ has also been considered in both cases.

As regards the homopolymer blends A and B, it has been shown that the effective screened potential $U^s_{AA,H}$ is sensitive to the composition $\Phi_A$ in the mixture. In the small $\Phi_A$ range, when $\chi_F N$ increases, $U^s_{AA,H}$ changes sign and becomes negative (attractive) before the system reaches the phase separation ($|U^s_{AA,H} \rightarrow \infty$), which occurs for the value of $\chi_F N = 2$ at $\Phi_A = 0.5$. The situation is different in the high-$\Phi_A$ regime. Indeed, the effective screened potential is always positive (repulsive) and this is probably due to the high quantity of species A present within the mixture. Because of the symmetry of the system, the Gaussian behavior of the A chain is, in this case, transferred to the B species.

As far as the **k** dependence is concerned in both cases, the result is in perfect agreement with the theoretical approach dealing with the scattering properties.[2-5] Indeed, it has been shown that before the spinodal is reached ($|U^s{}_{AA,H}| \rightarrow \infty$), in the case of the blend of homopolymers A and B (50/50), the effective screened potential goes to zero for $(\chi_F N)_0 = 1$ (Gaussian behavior), becomes negative for $1 < \chi_F N < 2$, and finally diverges at $(\chi_F N)_c = 2$. This situation occurs at the value of $|\mathbf{k}| = 0$. In the case of diblock copolymer A–B (50/50), the variation of the screened potential $U^s{}_{AA,C}$ discloses similar behavior at the value of $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$. When $\chi_F N$ increases, $U^s{}_{AA,C}$ vanishes at $(\chi_F N)_0 \simeq 3.4$ and becomes negative (attractive) for $\chi N > (\chi N)_0$ until the system reaches microphase separation, which occurs at $(\chi_F N)_c = 5.25$. These values of $|\mathbf{k}^*|$ and $(\chi_F N)_c$, for both systems studied in this paper, namely, the blend of two homopolymers A and B and diblock copolymer A–B, are identical with those calculated by Leibler.[2]

Let us discuss the size for the 50/50 block copolymer qualitatively. The size of the A block would be crudely given by

$$\langle R_A{}^2\rangle \approx N_A l^2 \left\{1 + \int \frac{d^3\mathbf{k}}{N_A \mathbf{k}^2} U^s{}_{AA,C}(\mathbf{k})\right\} \qquad (60)$$

where $l$ is the effective step length of the copolymer chain. Unfortunately, the integral cannot be calculated analytically. As we see from eq 54, the screened potential changes sign before microphase separation of $|\mathbf{k}|$ values around $|\mathbf{k}^*|$. Thus we would expect a similar behavior as shown for the homopolymer blends; i.e., it shrinks before microphase separation takes place. An equation similar to eq 60 holds for the B part of the copolymer. The dominant contribution of the integral comes from $|\mathbf{k}| = |\mathbf{k}^*|$, and we expect the B part to shrink before the microphase separation. Thus we expect the whole block copolymer to shrink.

In this paper we treated the fluctuations in Gaussian approximation. For the homopolymer blend this is not valid near the critical point and higher order should be taken into account. For a clear discussion of the effect of fluctuations near the microphase separation in symmetric diblock copolymer, see the paper of Fredrickson and Helfand.[11]

**Acknowledgment.** We thank reviewer I for interesting comments on this work. R.B. gratefully acknowledges the support of the Max-Planck-Gesellschaft and thanks Professor E. W. Fischer for his invitation to work at the Max-Planck-Institut für Polymerforschung in Mainz.

## Appendix

In this Appendix, we give a simple and general formula for the effective screened potential deduced from the binary homopolymer A/solvent case. In the latter, one knows that the structure factor $S_{AA}(\mathbf{k})$ is

$$1/S_{AA}(\mathbf{k}) = 1/S_{AA}{}^0(\mathbf{k}) + V \qquad \text{(A-1)}$$

where $S_{AA}{}^0(\mathbf{k})$ is the "bare" structure factor and $V$ the excluded volume. The effective screened potential is given by[10]

$$U^s{}_{AA} = [1/S_{AA}{}^0(\mathbf{k}) + V] - V^2/[1/S_{AA}{}^0(\mathbf{k}) + V] \qquad \text{(A-2)}$$

After straightforward algebraic operations, one obtains a general expression for the effective screened potential

$$U^s{}_{AA} = 1/S_{AA}{}^0(\mathbf{k})[1 - S_{AA}(\mathbf{k})/S_{AA}{}^0(\mathbf{k})] \qquad \text{(A-3)}$$

The use of this formula in the general case is well justified since starting from the complete Hamiltonian for the binary blend case,[1] $U^s{}_{AA}$ has been found to be identical with relation A-3.

## References and Notes

(1) Brereton, M. G.; Vilgis, T. A. *J. Phys. (Les Ulis, Fr.)* **1989**, *50*, 245.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(3) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(4) Benmouna, M.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227.
(5) Benoit, H.; Koberstein, J.; Leibler, L. *Makromol. Chem. Suppl.* **1981**, *4*, 85.
(6) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1986**, *19*, 2501.
(7) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(8) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(9) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(10) Edwards, S. F. *J. Phys.* **1975** *A8*, 670.
(11) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.