Spinodal Shifts of a Polymeric Blend Film on an Interacting Surface

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ABSTRACT: We use the Gaussian chain model in half-space, to study surface interacting binary polymer blends for a system that is not laterally incompressible. We derive the partition function of the system to all orders of the surface interaction parameters and find the spinodal limits. Surface-spinodal lines are shifted from those of the bulk on changing the thickness of the film or surface interactions, due to the change of the average number of heterocontacts between the units of different kind. These heterocontacts generally decrease for opposite surface interactions of the two species and contribute to the stability of the blend while they increase for surface interactions of the same kind, leading to destabilization. We thus explain quantitatively the experimental observations of both positive and negative shifts of the spinodals of polymeric films. For large confinements, an increase of the stability of a film is seen. This agrees with what is found in polymer blends and mixtures of smaller molecules between two symmetrical surfaces by Monte Carlo techniques and mean and self-consistent field theories.

1. Introduction

The phase separation of polymer blends in films formed on a surface has found continually increasing research interest mainly because the stability and morphology of these blends are changed compared to those of the bulk,[1] due to the surface interactions and the confinement of the chains. Experimentally both tendencies of increasing but also of decreasing the stability of a film on different substrates have been observed.[2] Previous work, on polystyrene/poly(vinylmethyl ether) [PS/PVME] blend films on surfaces of gold and glass, with thicknesses smaller than 1 μm has demonstrated not only positive cloud-point shifts, indicating surface-induced mixing, but also negative shifts, indicating surface-induced demixing.[3] Followed on studies in polyvinyl acetate/poly(methyl methacrylate) [PVA/PMMA] films of various thicknesses found also positive and negative shifts on changing the substrate.[4] Lately in a work on ultrathin films of PS/PVME mixtures on hydrophilic SiO substrate, a large destabilization behavior on decreasing the film thickness has also been seen.[5] The width of the film in these experimental studies is at least 10 times larger than the size of a coil, and this permits the employment of half-space statistics with only one impenetrable surface that imitates the presence of the substrate, as we further explain in subsection 2B.

Theoretical treatments of polymer mixtures in finite geometries appeared only very recently, modeling the film by polymer mixtures confined by two equivalent neutral walls and studying surface boundary effects on the two phase coexistence. Both in a mean-field treatment of the Landau−Ginzburg free energy functional with surface contributions[6] and in Monte Carlo simulations,[7] the symmetric coexistence curves were found to be suppressed, explaining thus the increase of stability of a polymeric film. These symmetrical cases do not exactly reflect the experiments with a film on an impenetrable surface having its second surface open to the air. Beyond the stability found also for mixtures of small molecules between two symmetrical planes,[8,9] the explanation of the opposite behavior of the destabilization of a film remains. A theory is necessary that is capable to determine the conditions for not only the increase but also the decrease of the stability of a film that have also to be seen by Monte Carlo techniques in systems of small molecules with specific interactions.[9] The specific surface−segment interactions, the space confinement, the segment−segment interactions, and the molecular weights of the two components all play a decisive role and are closely related to the criticality.

In this work we employ an Edward's type Hamiltonian and half-space statistics,[10] where the chains are considered continuous lines each one having a contour length N in dimensionless units, proportional to the molecular weight of the polymer. We study the case of two different kinds of linear flexible polymer chains labeled as a and b, respectively, interacting between them, and with an impenetrable reflecting surface. We derive the partition function and the free energy of the system, directly related to the chemical potentials of the two species and we search for the effects of the surface interactions on stability. We do this by exploring the dependence of the spinodal curves of the interacting polymer mixture on the surface interactions, the molecular weights of the two polymers and the film thickness. Any interplay with wetting and prewetting transitions often observed[11] and related with the interactions of the two polymers with the substrate, is considered for simplicity to be absent. While the surface and the width of the film can both vary in certain series of experiments we will confine ourselves to the cases where the width of the film is kept constant. In these cases of lateral changes that permit the study of systems not laterally incompressible the calculations are simpler. In the next section the model is presented starting in subsection 2A with the partition function in half-space and explaining in subsection 2B the effects of confinement. In section 3 we find the free energy of the system, and we derive the expression of the spinodal. Analytical results are presented in section 4, and in section 5 we end with the conclusions.

2. The Model

2A. The Partition Function. The configurational partition function in an ensemble of n_a and n_b chains of

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the two species, interacting with each other and with a planar impenetrable wall at $z = 0$, is given by

$$Z = \frac{1}{n_a! n_b!} \int D[r] \prod_{k=1}^{n_a} \prod_{\lambda=1}^{n_b} P_o[r(\tau_k)]\, P_o[r(\tau_\lambda)] \times \exp\{-\, u_{a'} \int_0^{N_a l_a} \delta[z(\tau_k)]\, d\tau_k - u_{b'} \int_0^{N_b l_b} \delta[z(\tau_\lambda)]\, d\tau_\lambda - w \int_0^{N_a l_a} \int_0^{N_b l_b} \delta[r(\tau_k) - r(\tau_\lambda)]\, d\tau_k\, d\tau_\lambda\} \quad (2.1)$$

$D[r]$, in eq 2.1, stands for the functional integration of the position vectors of all chain points over the whole volume $V = S \times L$, where S is the surface area and L the length of the perpendicular dimension along the positive z axis. The ideal probability chain distribution

$$P_o[r(\tau_i)] = \exp\left\{ -\frac{3}{2 l_i^{\,2}} \int_0^{N_i l_i} \left| \frac{dR(\tau_i)}{d\tau_i} \right|^2 d\tau_i \right\} \quad (i = \kappa, \lambda) \quad (2.2)$$

corresponds to space curves $r(\tau_i)$ of type $i = \kappa, \lambda$ with τ_κ and τ_λ being the contour lengths in dimensionless units of the a and b chains, respectively. l_i is the statistical segment length and N_i is the contour length of the i*th* chain proportional to the number of monomer units of each chain. Though possible, no specific analysis on the lengths of the two units is included in this work so for simplicity from now on the two unit lengths will be considered equal $l_a = l_b = l$, both of them taking the value one, $l = 1$. The interaction parameter w is equal to half the binary cluster integral of the average potential between the units of different chains, while $u_{a'}$ and $u_{b'}$ are the binary cluster integrals of the mean potentials between the units of the a and b chains and the surface. The appropriate reflecting boundary conditions ensure the impenetrability of the surface describing thus an interacting impenetrable surface boundary[12] and the possibility of the chains to belong to the right half-space of volume $V = S \times L$. A second surface is not included at the free surface of the film, which is in touch with the air. We explain in section 2B how these half-space statistics can describe the film behavior when the film's width is larger than the chain size. As far as the w interactions are concerned, we work in a perturbation theory scheme where only open diagrams are taken into account, and this is equivalent to the random phase approximation. In this approximation though Z includes terms to all orders of w they sum up to an exponential giving a free energy $F/KT = -\ln[Z]$, which contains terms up to first order in w only. This form of the free energy without the surface interactions ($u_a{}'$, $u_b{}' = 0$), together with the filling of the available volume V with monomer units

$$V = (n_a N_a + n_b N_b) v_o \quad (2.3)$$

is the same with that of the Flory–Huggins approximation.[13] The volume v_o occupied by each unit is considered for simplicity to be the same for the two different kinds of units and equal to unity. The final solution takes also into account the surface interactions with the impenetrable surface to all orders of the parameters $u_{a'}$ and $u_{b'}$, considering thus the whole range of their intensities. While in partially miscible polymer blends the effective w interactions related to heterocontacts and responsible for unmixing is much smaller than unity ($wN \leq 2$) there is no reason to assume that interactions between the monomer units and the surface are similarly small. Though these interactions are considered insensitive to temperature, they are analyzed to all their range of definition from $-\infty$ to $+\infty$ in order to describe all the cases of different interactions with the substrates. At this point, one must realize that this approach disregards the special dependence of the Flory parameter on composition and chain architecture that arises from many-body chain correlations.[14] Beyond this point, no other approximation is used, since the final analytic solution sums all diagrams in the diagrammatic expansion of the surface interaction parameters u_a and u_b, as we have done for the study of the amounts of the two species adsorbed at the substrate, following methods previously established.[15]

The partition function Z of eq 2.1 can be written to order w, in terms of the partition functions of the pure components interacting with the surface, namely Z_a and Z_b respectively,

$$Z_i = \int D[r]\, P_o[r(\tau_i)] \exp\{-\, u_{a'} \int_0^{N_i l_i} \delta[z(\tau_i)]\, d\tau_i\} \quad (i = a,b) \quad (2.4)$$

and the partition function Z_{ab} of pairs of chains in contact, each pair interacting with the surface. The pair partition function is given by the functional integral

$$Z_{ab} = \int D[r] P_o[\{r(\tau_1)\}] P_o[\{r'(\tau_2)\}] \times \exp\{-\, u_{a'} \int_0^{N_a} \delta[z(\tau_1)]\, d\tau_1 - u_b{}' \int_0^{N_b} \delta[z'(\tau_2)]\, d\tau_2\} \int_0^{N_a} \int_0^{N_b} \delta[r(\tau_1) - r'(\tau_2)]\, d\tau_1\, d\tau_2\} \quad (2.5)$$

where the $\delta[r(\tau_1) - r'(\tau_2)]$ term describes the contact between the two chains of the pair. In the thermodynamic limit and to first order in the interaction parameter w, the free energy becomes

$$\frac{F}{KT} = -\ln Z = -n_a \ln\left[\frac{Z_a}{n_a}\right] - n_b \ln\left[\frac{Z_b}{n_b}\right] + w n_a n_b \frac{Z_{ab}}{Z_a Z_b} \quad (2.6)$$

and can be found after the calculation of Z_a, Z_b, and Z_{ab}.

The partition functions Z_a and Z_b have been given in a form of an exact analytic expression, found by means of integral equations and Laplace transforms, a technique that has been used for a long time.[16] They can be expressed in terms of the probability distributions $P_i(z,N_i)$ of a chain localized with one of its ends at a distance z from the impenetrable surface. $P_i(z,N_i)$ has been given before[16] and its Laplace transform is given by

$$\bar{P}_i(z,s_i) = \int_0^\infty dN_i \exp(-\, s_i N_i) P_i(z,N_i) = \frac{1}{s_i} - u_i \frac{\exp\{-6^{1/2} z (s_i)^{1/2}\}}{s_i((s)^{1/2} + u_i)}, \quad u_i = u_{i'}({}^3/{}_2)^{1/2} \quad (2.7)$$

This gives for Z_i in Laplace space the form

$$\bar{Z}_i = \int dx \int dy \int_0^\infty dz\, P_i(z,s_i) = V\left(\frac{1}{s_i} + \frac{\bar{K}_i}{L}\right) \quad (2.8)$$

with

$$\bar{K}_{\mathrm{i}} = -\frac{u_{\mathrm{i}}}{6^{1/2}s_{\mathrm{i}}^{3/2}(s_{\mathrm{i}}^{1/2} + u_{\mathrm{i}})}$$

where the double integral $\int \mathrm{d}x \int \mathrm{d}y$ yields the surface S of the film. Finding the inverse Laplace transform, Z_{i} becomes equal to

$$Z_{\mathrm{i}} = \mathrm{V}\left(1+\frac{K_{\mathrm{i}}}{L}\right), \quad (\mathrm{i} = \mathrm{a,b}),$$

$$K_{\mathrm{i}}(U_{\mathrm{i}},R_{\mathrm{i}},L) = -R_{\mathrm{i}}\left\{\frac{2}{\sqrt{\pi}} - \frac{1}{U_{\mathrm{i}}} + \frac{1}{U_{\mathrm{i}}}\exp(U_{\mathrm{i}}^2)\,\mathrm{erfc}(U_{\mathrm{i}})\right\}, \quad (\mathrm{i} = \mathrm{a,b}), \quad (2.9)$$

where V is the volume and $R_{\mathrm{i}} = (N_{\mathrm{i}}/6)^{1/2}$ are the radii of gyration of the unperturbed chains. $U_{\mathrm{i}} = u_{\mathrm{i}}(N_{\mathrm{i}})^{1/2}$ are scaled surface interactions, $L = V/S$ the perpendicular dimension of the sample respectively, and erfc is the complementary error function.

2B. Confinement. A thing to notice is that the $1/s_{\mathrm{i}}$ term of eqs 2.7 and 2.8 comes from the unity which reflects the normalization of the probability distribution of a chain confined in the half-space. Though a second image term from reflection is included in this probability, the integration in the region of the half-space where it is defined furnishes unity. Actually as can be shown from the works in ref 17, the same normalization is true even in the case of the existence of two impenetrable reflecting surfaces at $z = 0$ and $z = L$ where all infinite number of reflections are taken into account. The rest u terms concern localized chains with one or more points at the surface. The employment of the half-space statistics for these localized configurations actually considers negligible all reflections of the probability distribution from a second impenetrable reflecting surface at L, which is not a bad approximation. As is known,[17] the reflections of the next generations are exponentially decaying and for L larger than the size of the coils, which is what happens in a film of width of several radii of gyration of the chains, are certainly negligible. The smaller contributions of these localized configurations lead to a division with L appearing in all terms of nonzero u. A final check of the validity of the method in certain regions of the parameters can be done from the requirement that the partition functions and the number $\langle\delta_{\mathrm{ij}}\rangle$ of heterocontacts (eq 3.3), coming after the summation of all u terms, must be positive. We will see in the following analysis that these limits are different depending on the state of the chains determined from the values of the two u's. For the case of u's > 0 where the chains are expanded, larger L's are necessary for the model to be valid, while for u's < 0, where the extension of the coils out of the surface reduces, the final expressions enlarge their regions of definition to smaller values of L. We manage thus to describe films of blends by means of half-space statistics, without having to employ more complex systems of mixtures of polymers between two impenetrable surfaces with the same or different interaction parameters.[18]

Because of the presence of $\delta[r(\tau_1) - r'(\tau_2)]$ in eq 2.5 which brings in contact two points of two chains of different kind, Z_{ab} describes a system of four chain parts starting from a common point at z and having their ends free. It can therefore be expressed as the integral over z of the probability of these four chain parts and it is given by

$$Z_{\mathrm{ab}} = \int \mathrm{d}x \int \mathrm{d}y \int_0^{\infty} \mathrm{d}z \int_0^{N_{\mathrm{a}}}\int_0^{N_{\mathrm{b}}} \mathrm{d}\tau_{\mathrm{a}}\,\mathrm{d}\tau_{\mathrm{b}}\, P_{\mathrm{a}}(z,\tau_{\mathrm{a}}) \times P_{\mathrm{a}}(z, N_{\mathrm{a}} - \tau_{\mathrm{a}})P_{\mathrm{b}}(z,\tau_{\mathrm{b}})P_{\mathrm{b}}(z,N_{\mathrm{b}} - \tau_{\mathrm{b}}) \quad (2.10)$$

The two P_{a}'s and the two P_{b}'s in eq 2.10 are of the convolution type and their double Laplace transform over N_{a} and N_{b} with Laplace transforms s_{a} and s_{b} respectively are simple products and can be evaluated by means of the expression eq 2.7. Z_{ab} obtains the form

$$\begin{aligned} Z_{\mathrm{ab}} &= \mathrm{V}\, L_{\mathrm{a}}^{-1}L_{\mathrm{b}}^{-1} \int_0^{\infty} \mathrm{d}z\, \bar{P}_{\mathrm{a}}(z,s_{\mathrm{a}})^2\bar{P}_{\mathrm{b}}(z,s_{\mathrm{b}})^2 \\ &= \mathrm{V}L_{\mathrm{a}}^{-1}L_{\mathrm{b}}^{-1}\left\{\frac{1}{s_{\mathrm{a}}^2 s_{\mathrm{b}}^2} + \frac{\bar{K}_{\mathrm{ab}}(s_{\mathrm{a}},s_{\mathrm{b}})}{L}\right\} \\ &= \mathrm{V}\left\{N_{\mathrm{a}}N_{\mathrm{b}} + \frac{K_{\mathrm{ab}}}{L}\right\} \end{aligned}$$

with L_{a}^{-1} and L_{b}^{-1} the a and b inverse Laplace transforms and

$$\begin{aligned} 6^{1/2}\,\bar{K}_{\mathrm{ab}}(s_{\mathrm{a}},s_{\mathrm{b}}) = &-\frac{2u_{\mathrm{a}}}{s_{\mathrm{a}}^{5/2}(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})s_{\mathrm{b}}^2} + \\ &\frac{u_{\mathrm{a}}^2}{2s_{\mathrm{a}}^{5/2}(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})^2 s_{\mathrm{b}}^2} - \frac{2u_{\mathrm{b}}}{s_{\mathrm{b}}^{5/2}(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})s_{\mathrm{a}}^2} + \\ &\frac{u_{\mathrm{b}}^2}{2s_{\mathrm{b}}^{5/2}(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})^2 s_{\mathrm{a}}^2} + \\ &\frac{4u_{\mathrm{a}}u_{\mathrm{b}}}{s_{\mathrm{a}}^2(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})s_{\mathrm{b}}^2(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})(s_{\mathrm{a}}^{1/2} + s_{\mathrm{b}}^{1/2})} - \\ &\frac{2u_{\mathrm{a}}^2u_{\mathrm{b}}}{s_{\mathrm{a}}^2(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})^2 s_{\mathrm{b}}^2(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})(2s_{\mathrm{a}}^{1/2} + s_{\mathrm{b}}^{1/2})} - \\ &\frac{2u_{\mathrm{b}}^2u_{\mathrm{a}}}{s_{\mathrm{b}}^2(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})^2 s_{\mathrm{a}}^2(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})(2s_{\mathrm{b}}^{1/2} + s_{\mathrm{a}}^{1/2})} + \\ &\frac{u_{\mathrm{a}}^2u_{\mathrm{b}}^2}{s_{\mathrm{a}}^2(s_{\mathrm{a}}^{1/2} + u_{\mathrm{a}})^2 s_{\mathrm{b}}^2(s_{\mathrm{b}}^{1/2} + u_{\mathrm{b}})(s_{\mathrm{a}}^{1/2} + s_{\mathrm{b}}^{1/2})} \end{aligned} \quad (2.11)$$

$\bar{K}_{\mathrm{ab}}(s_{\mathrm{a}},s_{\mathrm{b}})$ in eq 2.11 is a function of the surface interaction parameters u_{a} and u_{b}, and the two Laplace variables, s_{a} and s_{b}, conjugate to N_{a} and N_{b} respectively. Its double inversion yields Z_{ab} in the form $Z_{\mathrm{ab}} = V\{1 + K_{\mathrm{ab}}/L\}$ which by means of eq 2.6 and the expressions of Z_{a} and Z_{b}, in eq 2.9, furnish the partition function Z and the free energy. Within this direct solution we can now normally proceed with the thermodynamic calculations.

3. The Free Energy and the Spinodal

Because of the presence of the x, y plane the system of the polymers and the surface is not isotropic but has a cylindrical symmetry along the z direction. This symmetry is transferred to the free energy which after the substitution of Z_{a}, Z_{b}, and Z_{ab}, has the form

$$\begin{aligned}\frac{F}{KT} &= -\ln[Z] = -n_{\mathrm{a}}\ln\left(\frac{V+SK_{\mathrm{a}}}{n_{\mathrm{a}}}\right) - n_{\mathrm{b}}\ln\left(\frac{V+SK_{\mathrm{b}}}{n_{\mathrm{b}}}\right) + \mathrm{w}n_{\mathrm{a}}n_{\mathrm{b}}\frac{(VN_{\mathrm{a}}N_{\mathrm{b}}+SK_{\mathrm{ab}})}{(V+SK_{\mathrm{a}})(V+SK_{\mathrm{b}})}\\ &= -n_{\mathrm{a}}\ln\left[\frac{V}{n_{\mathrm{a}}}\left(1+\frac{K_{\mathrm{a}}}{L}\right)\right] - n_{\mathrm{b}}\ln\left[\frac{V}{n_{\mathrm{b}}}\left(1+\frac{K_{\mathrm{b}}}{L}\right)\right] + w\,\frac{n_{\mathrm{a}}n_{\mathrm{b}}}{V}\,\frac{\left(N_{\mathrm{a}}N_{\mathrm{b}}+\frac{K_{\mathrm{ab}}}{L}\right)}{\left(1+\frac{K_{\mathrm{a}}}{L}\right)\left(1+\frac{K_{\mathrm{b}}}{L}\right)}\end{aligned} \tag{3.1}$$

and depends on both parameters the volume V and the surface S and through them on the width of the film $L = V/S$. For a complete filling of the volume with monomers of the two different kinds, each one having a volume v_{a} and v_{b} respectively, the total volume is equal to $V = n_{\mathrm{a}}N_{\mathrm{a}}v_{\mathrm{a}} + n_{\mathrm{b}}N_{\mathrm{b}}v_{\mathrm{b}}$. For simplicity, we consider the two unit volumes v_{a} and v_{b} to be equal to unity, causing $V = n_{\mathrm{a}}N_{\mathrm{a}} + n_{\mathrm{b}}N_{\mathrm{b}}$ to appear dimensionless though it has the units of volume. This filling of the volume, with the monomers occupying a volume v_{i} each, is a simple extensivity relation, and it is not equivalent to the strict incompressibility relation that forces the sum of the concentrations of the two species to be constant everywhere and on the surface. The soft potentials which we use permit the two concentrations to vary independently, yielding a proper description of problems with various degrees of adsorption and depletion of the two species.[15] The free energy F of eq 3.1, is a function homogeneous to the first degree in the masses n_{a} and n_{b} and the area $S = V/L$ of the interface, $F(\lambda n_{\mathrm{a}},\lambda n_{\mathrm{b}},\lambda S) = \lambda\, F(n_{\mathrm{a}},n_{\mathrm{b}},S)$, and it can thus be written generally as $F = n_{\mathrm{a}}(\partial F/\partial n_{\mathrm{a}}) + n_{\mathrm{b}}(\partial F/\partial n_{\mathrm{b}}) + S(\partial F/\partial S)$. Concentrating though on experiments with lateral changes where L is constant, we see from eq 3.1 that F becomes a homogeneous function of n_{a} and n_{b} only and can be written as $F = n_{\mathrm{a}}(\partial F/\partial n_{\mathrm{a}}) + n_{\mathrm{b}}(\partial F/\partial n_{\mathrm{b}})$. Things are simplified under this assumption of constant L, and it is easily seen from this expression that proportionality relations exist among the three second derivatives $n_{\mathrm{a}}^2(\partial^2F/\partial n_{\mathrm{a}}^2) = n_{\mathrm{b}}^2(\partial^2F/\partial n_{\mathrm{b}}^2) = -\, n_{\mathrm{a}}n_{\mathrm{b}}(\partial^2F/\partial n_{\mathrm{a}}\partial n_{\mathrm{b}})$. The stability condition requires the second-order differential of the free energy to be nonnegative for all states near the equilibrium state, so that $(\partial^2F/\partial n_{\mathrm{a}}^2)\mathrm{d}n_{\mathrm{a}}^2 + 2(\partial^2F/\partial n_{\mathrm{a}}\partial n_{\mathrm{b}})\mathrm{d}n_{\mathrm{a}}\mathrm{d}n_{\mathrm{b}} + (\partial^2F/\partial n_{\mathrm{b}}^2)\mathrm{d}n_{\mathrm{b}}^2 \geq 0$. The equality which represents the border of stability, after the substitution of the rest of the second-order derivatives in terms of $\partial^2F/\partial n_{\mathrm{a}}^2$, is of the form $(\partial^2F/\partial n_{\mathrm{a}}^2)\partial n_{\mathrm{a}}^2(dn_{\mathrm{a}}/n_{\mathrm{a}} - dn_{\mathrm{b}}/n_{\mathrm{b}})^2 = 0$ and provides the spinodal curves

$$\partial^2F/\partial n_{\mathrm{a}}^2 = 0,\quad \text{spinodal for } L \text{ constant} \tag{3.2}$$

This criterion for the stability border is identical to that of homogeneous systems where F is also a homogeneous function of first degree to n_{a} and n_{b}. By means of eq 3.1, the free energy of the system can be expressed in terms of the average number $\langle\delta_{\mathrm{ij}}\rangle$ of heterocontacts between the two different chains, as

$$\begin{aligned}\frac{F}{KT} &= -\ln Z = -n_{\mathrm{a}}\ln V - n_{\mathrm{a}}\ln\left(1+\frac{K_{\mathrm{a}}}{L}\right) + n_{\mathrm{a}}\ln n_{\mathrm{a}} - n_{\mathrm{b}}\ln V - n_{\mathrm{b}}\ln\left(1+\frac{K_{\mathrm{b}}}{L}\right) + n_{\mathrm{b}}\ln n_{\mathrm{b}} + w\,\frac{n_{\mathrm{a}}n_{\mathrm{b}}}{V}\langle\delta_{\mathrm{ij}}\rangle,\\ \langle\delta_{\mathrm{ij}}\rangle &= \frac{\left(N_{\mathrm{a}}N_{\mathrm{b}}+\frac{K_{\mathrm{ab}}}{L}\right)}{\left(1+\frac{K_{\mathrm{a}}}{L}\right)\left(1+\frac{K_{\mathrm{b}}}{L}\right)}\end{aligned} \tag{3.3}$$

and it is indeed a function homogeneous to first order in n_{a} and n_{b} for constant L but varying S, describing thus systems not laterally incompressible.

Notice that for infinite thickness ($L \to \infty$) and because of the vanishing surface-to-volume ratio $S/V = 1/L \to 0$, $\langle\delta_{\mathrm{ij}}\rangle \to N_{\mathrm{a}}N_{\mathrm{b}}$, and the behavior of the system goes to that of the bulk. The free energy, eq 3.3, reduces in this limit to the familiar equation of the bulk where surface thermodynamics are negligible. In the case of a thin film, however, the ratio $L = V/S$ is not small, but it approaches the size of several (about 10) coils, the surface free energy contribution to the total free energy is significant, and consequently, every change in the surface state of the film leads to a change of its thermodynamic functions as well. By means of eqs 3.3, we can draw the spinodal curves $w(\varphi_{\mathrm{b}})$, and show the influence of the surface interactions on the mixture thermodynamics which in the present effort concerns a partially miscible mixture of two mutually repulsive polymer species. The spinodal is given by the line eq 3.2, which employing eq 3.3 leads to

$$2w\frac{\langle\delta_{\mathrm{ij}}\rangle}{N_{\mathrm{a}}N_{\mathrm{b}}} = \frac{1}{N_{\mathrm{a}}\Phi_{\mathrm{a}}} + \frac{1}{N_{\mathrm{b}}\Phi_{\mathrm{b}}},\quad \text{spinodal} \tag{3.4}$$

and it differs from the classical Flory spinodal in the fact that w is multiplied by the average number of contacts $\langle\delta_{\mathrm{ij}}\rangle$ between different monomers. In the bulk, $\langle\delta_{\mathrm{ij}}\rangle = N_{\mathrm{a}}N_{\mathrm{b}}$ and the Flory result is recovered. Increasing this average number of heterocontacts reduces w and the stability of the film decreases, while decreasing the average number of heterocontacts increases the stability of the film. It is through this quantity $\langle\delta_{\mathrm{ij}}\rangle$ which the influence of the surface on the spinodal is realized. It depends on the interaction parameters u_{a} and u_{b}, the width of the film L, and the two molecular weights N_{a} and N_{b}. This dependence comes through eq 3.3, from the quantities K_{a}, K_{b}, and K_{ab} given in the relations in eqs 2.9 and 2.11. The inversion of the double Laplace transforms of $\bar{K}_{\mathrm{ab}}(s_{\mathrm{a}},s_{\mathrm{b}})$ of eq 2.11 is tedious, but it can be done in a numerical way or up to certain integrals.[19] Despite this possibility we think that analytic solutions at certain limits of the interaction parameters u_{a} and u_{b} will provide a clear picture of the main effects, which do not depend solely on the difference $u_{\mathrm{a}} - u_{\mathrm{b}}$. In what follows, three specific limits of each interaction parameter u_{i} (i = a, b), in total six combinations, will be presented. We will study the limits of small u_{i} representing the weak interaction limit, the limits of large positive u_{i} describing the strong depletion of the species, and the limits of large negative u_{i} values describing the strong adsorption of the chains. In the rest three combinations we have different kinds of interactions between the two species, strong adsorption of the one species with strong depletion or weak interactions of the second, and strong depletion of the first species with weak interactions of the second.

4. Regions of Specific Interactions

4A. Weak Interaction Region. In the region of weak interactions, the interaction parameters u_a and u_b are small and an expansion of $\bar{K}_{ab}(s_a,s_b)$ to various orders of u_a and u_b can be done. To second order in u_a, u_b including the u_a^2, u_b^2, and the $u_a u_b$ terms, we obtain from eq 2.11 the expression

$$6^{1/2}\,\bar{K}_{ab}(s_a,s_b) = -\frac{2u_a}{s_a^{\,3}s_b^{\,2}} + \frac{5}{2}\frac{u_a^{\,2}}{s_a^{\,7/2}s_b^{\,2}} - \frac{2u_b}{s_b^{\,3}s_a^{\,2}} + \frac{5}{2}\frac{u_b^{\,2}}{s_b^{\,7/2}s_a^{\,2}} + \frac{4u_a u_b}{s_a^{\,5/2}s_b^{\,5/2}(s_a^{\,1/2}+s_b^{\,1/2})} \quad (4.1)$$

which includes five terms. The first four are simple powers and their inverse Laplace transforms are trivial, while that of the fifth is derived in the Appendix. Using also the second-order expression for K_a and K_b, from eq 2.9, $\langle\delta_{ij}\rangle$ of eq 3.3 takes the form

$$\langle\delta_{ij}\rangle = N_aN_b\left\{1 + \frac{1}{6^{1/2}L}\left[-u_aN_a + \frac{4}{3\pi^{1/2}}u_a^{\,2}N_a^{\,3/2} - u_bN_b + \frac{4}{3\pi^{1/2}}u_b^{\,2}N_b^{\,3/2} + \frac{64}{105\pi^{1/2}}u_au_b\left[\frac{(N_a+N_b)^{7/2}}{N_aN_b} - \frac{N_a^{\,5/2}}{N_b} - \frac{N_b^{\,5/2}}{N_a} - \frac{7}{2}(N_a^{\,3/2}+N_b^{\,3/2})\right]\right]\right\}\Bigg/ \left\{\left\{1 + \frac{1}{6^{1/2}\mathrm{L}}\left[-u_aN_a + \frac{4}{3\pi^{1/2}}u_a^{\,2}N_a^{\,3/2}\right]\right\}\left\{1 + \frac{1}{6^{1/2}L}\left[-u_aN_a + \frac{4}{3\pi^{1/2}}u_a^{\,2}N_a^{\,3/2}\right]\right\}\right\} \quad (4.2)$$

which when expanded to first order in $1/L$, ends up as the relation eq 4.3

$$\langle\delta_{ij}\rangle = N_aN_b\left\{1 + \frac{1}{6^{1/2}L}\,\frac{64}{105\pi^{1/2}}u_au_b\left[\frac{(N_a+N_b)^{7/2}}{N_aN_b} - \frac{N_a^{\,5/2}}{N_b} - \frac{N_b^{\,5/2}}{N_a} - \frac{7}{2}(N_a^{\,3/2}+N_b^{\,3/2})\right]\right\} \quad (4.3)$$

Of course we have to mention that $\langle\delta_{ij}\rangle$ is a positive quantity and can never reach zero or negative values for all cases where the nonideal term is negative like in the case when $u_au_b < 0$. We will see that for large negative u's where the chains are adsorbed the region of validity of the general solution can be extended even to smaller values of L still of course larger than the size of the coils. By means of the ratio of the two molecular weights $r = N_b/N_a$ the number of average contacts can be written in this limit of small interactions as

$$\langle\delta_{ij}\rangle = N_aN_b\left[1 + 0.344\,\frac{R_a}{L}U_aU_bF_1(r)\right], \quad \text{weak interactions } U_a,\ U_b \to 0 \quad (4.4)$$

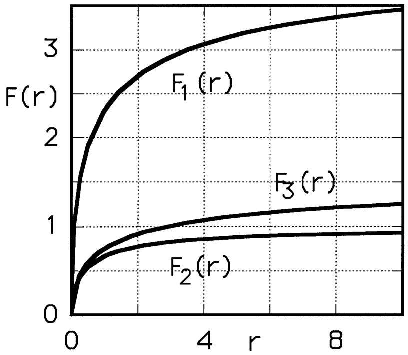

Figure 1. Functions F_1, F_2, and F_3 of eqs 4.4, 4.7, and 4.15. These are always positive and increase on increasing the ratio $r = N_a/N_b$ of the two different chains, indicating that larger dissimilarities of the two chains lead to more intense phenomena.

where

$$F_1(r) = \frac{(1+r)^{7/2}}{r^{3/2}} - \frac{1}{r^{3/2}} - r^2 - \frac{7}{2}\frac{1}{r^{1/2}} - \frac{7}{2}r,$$

$$r = \frac{N_b}{N_a}, \quad R_a = \left(\frac{N_a}{6}\right)^{1/2}, \quad U_a = u_aN_a^{\,1/2}$$

We plot in Figure 1 $F_1(r)$ as a function of the asymmetry ratio r and we see that it is always positive between the limits of $F_1(r) \to 0$ for $r \to 0$ to the value $F_1(r) \to {}^{35}/_{8} = 4.375$ for $r \to \infty$. This means that two regions can be realized where $\langle\delta_{ij}\rangle$ can be larger or smaller than the bulk value N_aN_b, depending on whether the product u_au_b is positive or negative, respectively. When u_a and u_b are of the same sign, indicating that both kinds of units are attracted or repulsed from the surface, $\langle\delta_{ij}\rangle$ is larger than the bulk value and the stability region of the film decreases, while when the interactions with the substrate are of opposite nature, the stability increases. This explains the experimental observations of the shifts of spinodals to both directions up or down depending on the nature of polymers and the substrate. This is what is seen in refs 2–5, where not only a decrease but also an increase of the two-phase region is observed. Two factors are found to affect the shifts of spinodals. As it is seen from eq 4.4 larger molecular weights cause larger changes to the bulk value $\langle\delta_{ij}\rangle = N_aN_b$ leading to an increase of the phenomena. Larger differences of the molecular weights of the two species, which increase the asymmetry ratio r, enhance also the phenomena. Because of both these factors the shifts of spinodals become more pronounced and ways for an easier detection of surface effects are thus predicted.

4B. Strong Interactions of the Same Kind. In the limit of strong repulsions of both species where both u_a, $u_b \to \infty$ $\bar{K}_{ab}(s_a,s_b)$ of eq 2.11 becomes

$$6^{1/2}\bar{K}_{ab}(s_a,s_b) = -\frac{3}{2}\frac{1}{s_a^{\,5/2}s_b^{\,2}} - \frac{3}{2}\frac{1}{s_b^{\,5/2}s_a^{\,2}} + \frac{9}{2}\frac{1}{s_a^{\,2}s_b^{\,2}(s_a^{\,1/2}+s_b^{\,1/2})} - \frac{2}{s_a^{\,2}s_b^{\,2}(2s_a^{\,1/2}+s_b^{\,1/2})} - \frac{2}{s_a^{\,2}s_b^{\,2}(s_a^{\,1/2}+2s_b^{\,1/2})} \quad (4.5)$$

On the basis of the inverse Laplace transform

$$L_a^{-1}L_b^{-1}\frac{1}{s_a^{2}s_b^{2}(s_a^{1/2}+s_b^{1/2})} = \frac{8}{15^{1/2}}\left[-(N_a+N_b)^{5/2}+N_a^{5/2}+N_b^{5/2}+\frac{5}{2}N_aN_b(N_a^{1/2}+N_b^{1/2})\right] \quad (4.6)$$

and the relation of the inverse Laplace transform $L^{-1}f(\lambda s) = (1/\lambda)F(N/\lambda)$, where $L^{-1}f(s) = F(N)$, all terms of $K_{ab}(s_a,s_b)$ can be inverted, leading to first order in $1/L$ to the expression

$$\langle\delta_{ij}\rangle = N_aN_b\left[1 + 1.128\,\frac{R_a}{L}\mathrm{F}_2(r)\right],$$

$$\text{strong repulsions } u_a,\ u_b \rightarrow \infty, \quad r = \frac{N_b}{N_a},$$

$$\mathrm{F}_2(r) = -\frac{6}{5}\frac{(1+r)^{5/2}}{r} + \frac{1}{15}\frac{(1+4r)^{5/2}}{r} + \frac{1}{15}\frac{(4+r)^{5/2}}{r} - \frac{1}{r} - r^{3/2} + r^{1/2} + 1 \quad (4.7)$$

We plot $F_2(r)$ in Figure 1 where we see that it obtains always positive values. It increases from the value 0 for $r \rightarrow 0$ to the value $F_2(r) \rightarrow 1$ for $r \rightarrow \infty$, indicating a small decrease of stability in this region of large repulsions of both species. This decrease of stability and of the mixing area of the two polymers increases when the difference of the molecular weights of the two species is larger.

Of interest is also the case of strong attractions of both species taken in the limit of both u_a, $u_b \rightarrow -\infty$. The most dominant contribution comes in this case from the last $u_a^2u_b^2$ term of eq 2.11. Useful in the evaluation of the inverse of this term is to replace the Laplace variables s_i (i = a, b) with $s_i = s_{i'} + u_i^2$, where $s_{i'} = s_i - u_i^2$. A dependence on $s_{i'}s$ is then taken, and the limit for $u_i \rightarrow -\infty$ or $|u_i| \rightarrow \infty$ is possible. Employing also the property $L_i^{-1}f(s_i - u_i^2) = \exp(u_i^2N_i)\ L_i^{-1}f(s_i)$, (i = a, b), we end up with the result $K_{ab} = [8N_aN_b/(|u_a| + |u_b|)]\exp(u_a^2N_a + u_b^2N_b)$ in this limit of strong attractions. K_a and K_b are similarly equal in this limit to $K_i = 2/|u_i|\exp(u_i^2N_i)$, (i = a, b), a relation also taken from their general expression eq 2.9. By means of these two expression the average number of contacts $\langle\delta_{ij}\rangle$ can be written as

$$\langle\delta_{ij}\rangle = N_aN_b\frac{1 + \dfrac{8\exp\{u_a^2N_a + u_b^2N_b\}}{6^{1/2}L(|u_a| + |u_b|)}}{\left[1 + \dfrac{2\exp\{u_a^2N_a\}}{6^{1/2}L|u_a|}\right]\left[1 + \dfrac{2\exp\{u_b^2N_b\}}{6^{1/2}L|u_b|}\right]} \quad (4.8)$$

For large L and in an expansion to first order in $1/L$, we take

$$\langle\delta_{ij}\rangle = N_aN_b\left[1 + 8\frac{R_a}{L}\frac{\exp\{U_a^2 + U_b^2\}}{(|U_a| + |U_b|r^{-1/2})}\right],$$

$$\text{large attractions } U_a,\ U_b \rightarrow -\infty \quad (4.9)$$

and we see that $\langle\delta_{ij}\rangle$ is larger than N_aN_b indicating a decrease of stability and an induction of unmixing in this limit of the same large attractions. The functions $\exp(U_i^2)$ yield large values for $U_i \rightarrow -\infty$, and this characterizes the region of large adsorptions. This strong exponential dependence taken when $u_i \rightarrow -\infty$ indicates a substantial reduction of the degree of compatibility in this region, explaining thus the large destabilization behavior found in ref 5.

The positive signs of the $1/L$ terms of eq 4.8 permit the extension to smaller values of L. This reflects the fact that both coils are adsorbed at the surface and in the limit $U_a, U_b \rightarrow -\infty$ of full adsorption of both species the extension of the chains in the perpendicular z direction is negligible and smaller than the small size L of the film. Of interest in this limit of small L and within the limitations of the model we see that the contribution of the second $1/L$ terms of eq 4.8 can be dominant, leading to the expression

$$\langle\delta_{ij}\rangle = N_aN_b\frac{2 \times 6^{1/2}L|u_a||u_b|}{|u_a| + |u_b|} \quad (4.10)$$

This causes $\langle\delta_{ij}\rangle$ to be smaller than the bulk value N_aN_b for $2 \times 6^{1/2}L|u_a||u_b|/|u_a| + |u_b| < 1$, indicating the possibility of an increase of stability at this limit of small L and large attractions. This explains the tendency to increase stability in thin films obtained by squeezing polymeric films between surfaces, seen also by mean field theories and Monte Carlo techniques.[6,7]

4C. Interactions of a Different Kind. Three different combinations of the u_a and u_b limiting values remain to describe all possibilities of the various regions of interactions that can be solved analytically. The first is the region of large attractions of the one species described by the limit of $u_a \rightarrow -\infty$ and small interactions of the second species described by the limit $u_b \rightarrow 0$. Making the substitution $s_a = s_{a'} + u_a^2$, finding the limit at $u_a \rightarrow -\infty$, and using the transformation $L^{-1}f(s_a - u_a^2) = \exp(u_a^2N_a)\ L_a^{-1}f(s_a)$ we end up to first order in u_b in the expression

$$\langle\delta_{ij}\rangle = N_aN_b\frac{1 + \dfrac{\exp\{u_a^2N_a\}}{6^{1/2}L|u_a|}\left(2 - \dfrac{16u_bN_b^{1/2}}{3\pi^{1/2}}\right)}{\left[1 + \dfrac{2\exp\{u_a^2N_a\}}{6^{1/2}L|u_a|}\right]\left[1 - \dfrac{u_bN_b}{6^{1/2}L}\right]} \quad (4.11)$$

For large L and to first order in $1/L$, we take the result

$$\langle\delta_{ij}\rangle = N_aN_b\left(1 - 3.01\frac{R_a}{L}\frac{U_b\exp(U_a^2)}{|U_a|}\right),$$

$$U_a \rightarrow -\infty, \quad U_b \rightarrow 0 \quad (4.12)$$

The general trend of increasing the stability when the interactions are of opposite nature and destabilizing the film when the interactions are of the same nature is followed in this case too. Indeed for u_b positive and opposite to u_a, the contribution to N_aN_b is negative and the stability of the film increases, while for u_b negative, the stability of the film decreases.

The second case is that of large attractions of one, e.g., the a species with $u_a \rightarrow -\infty$ and large repulsions of the b species with $u_b \rightarrow \infty$. Making the substitution $s_a = s_{a'} + u_a^2$, finding the limit at $u_a^2 \rightarrow \infty$, and using the transformation $L^{-1}f(s_a - u_a^2) = \exp(u_a^2N_a)\ L^{-1}f(s_a)$ again but taking also the limit $u_b \rightarrow \infty$ in this case, we end up with an expression in the limit of large L of the form

$$\langle \delta_{ij} \rangle = N_a N_b \left[1 - 2 \frac{R_a}{L} \frac{\exp(U_a^{\ 2})}{|U_a|} \right], \quad U_a \rightarrow -\infty, \quad U_b \rightarrow \infty \quad (4.13)$$

which indicates as expected that stability increases in this limit of opposite interactions.

For the final case of large a repulsions and weak b interactions $u_a \rightarrow -\infty$, $u_b \rightarrow 0$, we take

$$6^{1/2}\ \bar{K}_{ab}(s_a,s_b) = -\frac{3}{2} \frac{1}{s_a^{\ 5/2} s_b^{\ 2}} - \frac{2u_b}{s_b^{\ 3} s_a^{\ 2}} + \frac{4u_b}{s_a^{\ 2} s_b^{\ 5/2}(s_a^{\ 1/2} + s_b^{\ 1/2})} - \frac{2u_b}{s_a^{\ 2} s_b^{\ 5/2}(2s_a^{\ 1/2} + s_b^{\ 1/2})} \quad (4.14)$$

The first two inverse double Laplace transforms are trivial, and the third one is derived in the Appendix while the fourth can be found from the third and the transformation $L_a^{-1} f(4s_a) = 1/4\ F(N_a/4)$, giving finally the expression to order $1/L$

$$\langle \delta_{ij} \rangle = N_a N_b \left[1 + \frac{R_a}{L} U_b F_3(r) \right], \quad U_a \rightarrow \infty, \quad U_b \rightarrow 0,$$

$$F_3(r) = r^{1/2} - \frac{2}{3} r^{3/2} + \frac{8}{3\pi} + \frac{5}{4\pi} \frac{1}{r} - \frac{4}{3\pi} \frac{(1+r)^3}{r^{3/2}} \Bigg) \times \cos^{-1}[(1+r)^{-1/2}] + \frac{1}{24\pi} \frac{(1+4r)^3}{r^{3/2}} \Bigg) \cos^{-1}[(1+4r)^{-1/2}] \quad (4.15)$$

$F_3(r)$ is a positive function increasing between the limits $F_3(r) \rightarrow 0$ for $r \rightarrow 0$ to $F_3(r) \rightarrow {}^{16}/_{3}\pi = 1.698$ for $r \rightarrow \infty$. This quantifies again the general tendency of destabilizing the film for the same kinds of interactions and stabilizing it for opposite interactions.

5. Conclusions

The spinodal lines of a polymeric blend film are shifted from those of the bulk because of the interactions from the substrate and the confinement of the chains. These effects emerge when the surface S of the substrate is large and its ratio to the volume V of the film, $S/V = 1/L$ is not negligible. The possibility of stability decay indicates that phase separation can occur near surfaces even if the mixture in the bulk is stable. Contrary to this, the stability increase may lead to mixing in the surface area even if we have a two-phase behavior in the bulk.

We describe the effects of the surface interactions by means of two interaction parameters u_a and u_b. The values of u_a and u_b are proportional to the intensity of the surface interactions and can vary from $-\infty$ to $+\infty$ describing all cases from full attraction to full repulsions of polymeric units with the surface. Surface effects depend on the ratio R/L of the unperturbed radii of gyration R of the chains to the width L of the film and vanish on approaching large film thicknesses, when L is much larger than R and the spinodal curves merge into those of the bulk. The shifts of the surface driven spinodals are directly related to the average number $\langle \delta_{ij} \rangle$ of heterocontacts between different polymers and an analytic relation is derived which indicates that the stability region of the film is enhanced for smaller values of $\langle \delta_{ij} \rangle$. The general expression of film spinodals is given in the double Laplace space of the two lengths of the two different chains and analytical inversions in the cases of large or small interactions are analyzed. The solution reveals that generally opposite interactions with the substrate increase film's stability while interactions of the same kind lead to destabilization.

Both tendencies observed experimentally of increasing but also of decreasing the blend stability depending on the nature of the substrate are thus explained. In the specific case of ultrathin films where L is small and the interactions are very attractive, an increase of stability is found in accordance with what other theories and Monte Carlo enumerations find for the case of films squeezed to large confinements by means of two symmetrical walls. The cases of adsorption with large negative u_i yield strong effects of order $\exp(u_i N_i^2)$ while u_i positive yield functions of smaller value indicating weaker phenomena. This implies that for positive interactions when the species are depleted from the surface the surface effects are quite limited and a small decrease of stability is found while when at least one of the species is adsorbed larger shifts of the spinodals are expected. This explains the large destabilization effects which a surface can bring in certain cases. For larger molecular weights of the polymers the various trends become more pronounced and increasing the ratio of the molecular weights the intensity of the phenomena becomes also larger.

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Appendix

In this Appendix, we present examples of the evaluation of double inverse Laplace transforms. We start with the evaluation of $L_a^{-1} L_b^{-1}(1/s_a^{5/2} s_b^{5/2}(s_a^{1/2} + s_b^{1/2}))$ needed in eq 4.1. It is based on the double inverse Laplace transform $L_a^{-1} L_b^{-1}(1/s_a^{1/2} s_b^{1/2}(s_a^{1/2} + s_b^{1/2})) = 1/\pi^{1/2}(N_a + N_b)^{1/2}$, which can simply be proved in the straight Laplace transformation, equivalent to the double integral

$$\int_0^\infty \mathrm{d}N_a \exp(-s_a N_a) \int_0^\infty \mathrm{d}N_b \times \exp(-s_b N_b) \frac{1}{\pi^{1/2}(N_a + N_b)^{1/2}} = \frac{1}{s_a^{\ 1/2} s_b^{\ 1/2}(s_a^{\ 1/2} + s_b^{\ 1/2})}$$

Now

$$L_a^{\ -1} L_b^{\ -1} \frac{1}{s_a^{\ 5/2} s_b^{\ 5/2}(s_a^{\ 1/2} + s_b^{\ 1/2})} = L_a^{\ -1} L_b^{\ -1} \frac{1}{s_a^{\ 2} s_b^{\ 2}} \frac{1}{s_a^{\ 1/2} s_b^{\ 1/2}(s_a^{\ 1/2} + s_b^{\ 1/2})}$$

and because of the convolution property of Laplace transforms, we assume that

$$L_a^{\ -1} L_b^{\ -1} \frac{1}{s_a^{\ 5/2} s_b^{\ 5/2}(s_a^{\ 1/2} + s_b^{\ 1/2})} = \int_0^\infty dx_a (N_a - x_a) \int_0^\infty dx_b (N_b - x_b) \frac{1}{{}^{1/2}(x_a + x_b)^{1/2}}$$

The x_b integration is trivial, giving $L_a^{-1} L_b^{-1}[1/s_a^{5/2} s_b^{5/2}$

$(s_a^{1/2} + s_b^{1/2})] = (1/\pi^{1/2}) \int_0^\infty dx_a\, x_a[{}^4/_3(N_a + N_b - x_a)^{3/2} - 2N_b(N_a - x_a)^{1/2} - {}^4/_3(N_a - x_a)^{3/2}]$. An easy way to do the integrals of the three terms is to make the substitution $x_a = N\cos^2\varphi$ where $N = N_a + N_b$, for the first term and the substitution $x_a = N_a\cos^2\varphi$ for the remaining two. The integrals of the trigonometric functions are then straightforwardly solved, giving the result

$$L_a^{-1}L_b^{-1}\frac{1}{s_a^{5/2}s_b^{5/2}(s_a^{1/2}+s_b^{1/2})} = \frac{2^4}{3\times 5\times 7\pi^{1/2}}\Big[(N)^{7/2} - N_a^{7/2} - N_b^{7/2} - \frac{7}{2}N_aN_b(N_a^{3/2}+N_b^{3/2})\Big], \quad N = N_a + N_b$$

which is used in eq 4.1. The inverse double Laplace transform of eq 4.6 is also calculated along the same lines.

The evaluation of the inverse Laplace transform $L_a^{-1}L_b^{-1}[1/s_a^2s_b^{5/2}(s_a^{1/2} + s_b^{1/2})]$ necessary in eq 4.14 follows similar steps, leading to

$$L_a^{-1}L_b^{-1}\frac{1}{s_a^{2}s_b^{5/2}(s_a^{1/2}+s_b^{1/2})} = \frac{2}{\pi}\Big[\frac{8}{3}N^3\int_{cos^{-1}(N_a/N)^{1/2}}^{\pi/2}\cos^2\varphi\,\sin^4\varphi d\varphi - 4\,N_bN_a^2\int_0^{\pi/2}d\varphi\,\cos^2\varphi\,\sin^2\varphi - 8/3\,N_a^3\int_0^{\pi/2}d\varphi\,\cos^2\varphi\,\sin^4\varphi\Big]$$

which upon integrating the trigonometric functions, gives

$$L_a^{-1}L_b^{-1}\frac{1}{s_a^{2}s_b^{5/2}(s_a^{1/2}+s_b^{1/2})} = \frac{N_aN_b^2}{2} + \frac{N_b^3}{6} - \frac{1}{12\pi}\Big[-\frac{32}{3}N_a^{3/2}N_b^{3/2} + 4N_a^{1/2}N_b^{5/2} - 4\,N_a^{5/2}N_b^{1/2} + 4N^3\cos^{-1}(N_a/N)^{1/2}\Big]$$

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