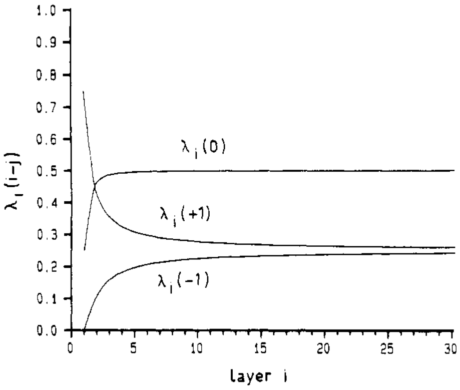

Figure 1. Fraction of neighbors of a site in layer i of a spherical lattice which are in the next layer, $\lambda_i(+1)$, in the same layer, $\lambda_i(0)$, and in the previous layer, $\lambda_i(-1)$, as a function of layer number V (hexagonal lattice).

proportional to the contact area this cell has with that layer, or

$$\lambda_i(+1)/\lambda_i(-1) = S_i/S_{i-1} \qquad \text{for all } i > 1 \tag{8}$$

where S_i stands for the contact area between layers i and $i + 1$. The number of lattice sites for layer i is given by the difference in volume of two spheres with a radius i and $i - 1$, respectively: $L(i) = V_i - V_{i-1}$. For a spherical lattice $V_i = {}^4/_3\pi i^3$ (in units of single cell volume) and the contact area between layers i and $i + 1$ is given by $S_i = 4\pi i^2$. The final result is

$$\lambda_i(+1) = \lambda(1)\frac{S_i}{L_i} \qquad \lambda_i(-1) = \lambda(1)\frac{S_{i-1}}{L_i}$$
$$\lambda_i(0) = 1 - \lambda_i(+1) - \lambda_i(-1) \tag{9}$$

for $i > 0$. The inversion symmetry requirement (eq 3) is met, as one can easily verify by using eq 7: in fact ω_c becomes totally invariant to the method of counting. It appears that according to our equations $\lambda_i(+1)$ and $\lambda_i(-1)$ are significantly different from their counterparts in a flat lattice, even for relatively large values of i (see Figure 1).

In conclusion, the model of Scheutjens and Fleer can be adapted to spherically symmetric systems in a consistent way by applying eq 9.

Acknowledgment. We thank Jan Scheutjens for helpful discussions.

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Received December 2, 1987

Reply to Comment on "Thermodynamics of the Separation of Biomaterials in Two-Phase Aqueous Polymer Systems: Effect of the Phase-Forming Polymers"

In order to investigate the behavior of biomaterials, specifically of proteins, in two-phase polymer solutions we have recently modified[1] Scheutjens and Fleer's liquid lattice model[2,3] for the adsorption of polymer chains to a flat surface. Since particles usually have nonplanar surfaces the adaptation consisted of recasting Scheutjens and Fleer's model in a lattice of given (usually variable) curvature around a curved surface. At the heart of such an endeavor is the choice of a functional form for the directional weighting factors, $\lambda_i(j - i)$, which are the geometrical weighting factors for placement of the next chain segment in layer j given that the present one is in layer i. We chose the physically intuitive form of the ratio between the number of sites in layer j to that in layer i. van der Schoot and Leermakers[4] now take issue with our treatment of curvature in this liquid lattice model; they have chosen[5] a different form for λ_i, specifically constructed to avoid the inconsistencies to which the earlier choice leads.

van der Schoot and Leermakers are correct when they note that the effect of the curvature of the lattice on the combinatorial factor (which describes the number of different ways of arranging the polymer chains and solvent molecules in the lattice) is attenuated by our approximating the directional weighting factors, λ_i, by a local geometric average (to ensure "inversion symmetry") and that in our treatment the computed number of segment–solvent contacts is only approximately equal to the number of solvent–segment contacts (i.e., that our[1] eq 14 does not strictly hold). van der Schoot and Leermakers point[4] to an alternate definition of λ_i, given by Leermakers, van der Schoot, Scheutjens, and Lyklema;[5] this new form (eq 9 in their paper) indeed satisfies the condition that the number of segment–solvent contacts must be equal to the number of solvent–segment contacts. Values for λ_i computed with their formulas are closer to those obtained for a planar lattice (i.e., the limiting values as $i \to \infty$) than those computed[6] with our[1] eq 5 by roughly a factor of 2 (for these comparisons, we set the radius of the spherical particle, R, to zero), and since the λ_i's enter not only into the calculations of the combinatorial factor but also into those of the system energy, a compensation takes place: the new model[4,5] is more sensitive to changing curvature than ours[1] in the combinatorial factor, but less so in the energy. Also, we find the appeal of this new definition for λ_i, which is based on a ratio of the surface area to the volume of the layer, somewhat tempered by its dimensional inconsistency.

To assess the effect that changing our definition of λ_i to that of Leermakers et al.[5] would have on the results reported in our paper,[1] we have recalculated most values reported earlier. It is comforting to be able to state that the changes in the calculated Gibbs energies are minimal. A plot of the Gibbs energy per particle as a function of the polymer–particle interaction parameter χ_s, computed with Leermakers et al.'s[5] as well as with our definitions for λ_i, is shown in Figure 1 (the case shown is identical with the one depicted in Figure 5 of the original paper[1]). Also, the slight influence of the change of formulas used for λ_i on the Gibbs energy is systematic, so that the values of the distribution coefficients between different phases are not perceptibly different. Since the results published earlier are not changed significantly, we are led to believe that the particle surface area and the volume of lattice sites in a layer, which are calculated identically in the two model

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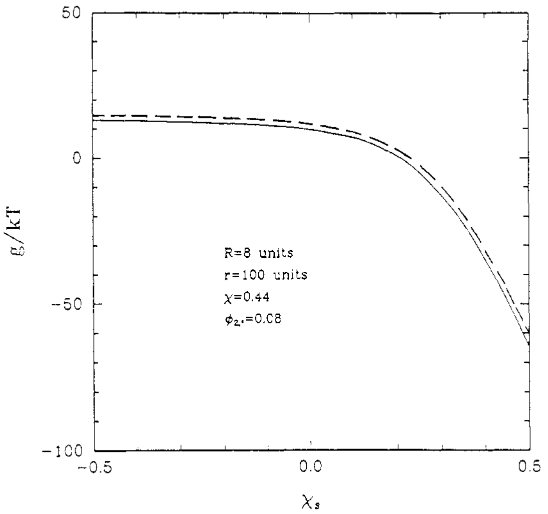

Figure 1. Gibbs energy per particle as a function of the polymer–particle interaction parameter χ_s; the solid line shows the results obtained with our definition of the directional weight factors λ_i (ref 1), the dashed line represents values obtained with the formulas of Leermakers, van der Schoot, Scheutjens, and Lyklema (ref 4 and 5).

formulations, are the major influences on the observed partitioning behavior.

Clearly, Leermakers et al.'s choice of function for λ_i is formally superior to the one we made, based on a physically intuitive appeal, and should be chosen for curved lattices without a solid particle at the center where the molecules can reach the origin. For the case where a particle blocks the center of the lattice, such as the one addressed in our paper,[1] the choice of formulas makes very little difference, and is essentially aesthetic: ours has, in our view, a more satisfying physical meaning, that of Leermakers et al. leads to a more consistent lattice model.

Erratum to the Original Paper. We would like to take this opportunity to correct an embarrassing set of mistakes in the original text. These mistakes are completely editorial in nature and have no bearing on the final equations or results but make for confusing reading.

Appendix III in the original text is blatantly incorrect, and eq 8 is ambiguous. The correct expression for the Helmholtz energy (eq III-1) for the phase containing the particle should be[7]

$$a = -kT \ln \Xi + n_1^{\mathrm{T}}\mu_1 + n_2^{\mathrm{T}}\mu_2 \qquad \text{(i)}$$

where n_1^{T}; n_2^{T} are the numbers of solvent molecules and polymer chains in the system and μ_1 and μ_2 are their respective chemical potentials. In a lattice of constant volume and pressure, changes in the Helmholtz energy will be equal to changes in the Gibbs energy. Since here both are referenced to the pure bulk components, $g^{\text{phase+particle}}$, the Gibbs energy for the phase with the particle, is also given by eq i. The derivation presented in Appendix III should read as follows.

The Gibbs energy of the "unperturbed" phase, i.e., the phase without the particle, is given by

$$g* = n_1^{\mathrm{T}}\mu_1 + n_2^{\mathrm{T}}\mu_2 \qquad \text{(ii)}$$

The Gibbs energy of the system *with* the particle is given by eq i above, so that the change in the Gibbs energy of the system upon addition of the particle, g^{excess}, may be written

$$g^{\text{excess}} = g^{\text{phase+particle}} - g* = -kT \ln \Xi \qquad \text{(iii)}$$

(g^{excess} here is the same as g in the main body of the text of the original paper.) Substituting eq 9 from the original paper

$$\Xi = \sum_{\{n_c\}} Q_{\{n_c\}} \exp[\textstyle\sum_i (L_i \phi_{1,i} \mu_1)/kT] \exp[\sum_i (L_i \phi_{2,i} \mu_2 / rkT)] \qquad (9)$$

for Ξ in eq iii above gives

$$g^{\text{excess}} = -kT \ln Q - \textstyle\sum_i (L_i \phi_{1,i} \mu_1) - \sum_i (L_i \phi_{2,i} \mu_2 / r) \qquad \text{(iv)}$$

Substituting eq 19, III-7, and III-8 from the original paper

$$-(\ln Q) = n_2 \ln \phi_{2,*} + \textstyle\sum_i n_{1,i} \ln \phi_{1,i} + \sum_i n_{2,i} \ln p_i + \Delta U/kT \qquad (19)$$

$$\mu_2/kT = 1 - \phi_{2,*} - r\phi_{1,*} + \ln \phi_{2,*} + r\chi\phi_{1,*}(1 - \phi_{2,*}) \qquad \text{(III-7)}$$

$$\mu_1/kT = 1 - \phi_{1,*} - \phi_{2,*}/r + \ln \phi_{1,*} + \chi\phi_{2,*}(1 - \phi_{1,*}) \qquad \text{(III-8)}$$

for Q, μ_1, and μ_2 in eq iv above gives eq 20 in the original paper. Note that g^{excess} here is equal to the total surface tension $\gamma A/kT$ as defined by Roe[8] and by Scheutjens and Fleer.[2]

Acknowledgment. We thank Dr. J. M. H. M. Scheutjens for providing us with a preprint of ref 5.

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(6) If we assume a sphere of radius $R = 0$ at the core of the lattice, the formulas of Leermakers et al. can be directly compared to ours. For the purpose of illustration we note that for values of i = 3, 5, and 10, respectively, their formulas yield values for $\lambda_i(+1)$ of 0.36, 0.31, and 0.28, respectively, while ours give 0.49, 0.37, and 0.31, respectively.
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Received February 19, 1988

Formation of a Surface Monolayer and a Built-Up Multilayer from a Well-Defined Amphiphilic Block Copolymer

In this report we show that a well-defined amphiphilic block copolymer (**3**), derived from poly(ethyl acrylate)-*block*-poly(styrene) (**2**), can be prepared by using the catalytic system of halo-containing macroinitiator **1** and manganese carbonyl ($Mn_2(CO)_{10}$) and that such an amphiphilic block copolymer readily forms a surface monolayer, which is strongly affected by poly(styrene) (PSt) chain length and by varying pH in subphase, and forms a built-up multilayer.

Langmuir–Blodgett (LB) films have received much attention in recent years due to the fact that the control of

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