our theta temperature defined by the condition $A_2 = 0$, i.e., $k\Theta/\epsilon \simeq 3.71$, is not very different from the theta temperature reported for the same model by McCrackin, Mazur, and Guttman, which is based on dimensional analysis of a single chain ($k\Theta/\epsilon = 3.64$).

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Theory of Inhomogeneous Polymers. Lattice Model for Solution Interfaces

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ABSTRACT: A lattice theory is developed to treat interfaces involving concentrated polymer solutions. The free energy is written in terms of the concentration profile and the anisotropy probabilities for polymer bond directions. Minimization of this free energy with appropriate constraints leads to formulas for the interfacial features. One of these constraints, unique to polymer systems, links the concentration profile to the bond anisotropy. Numerical results are presented in the following paper.

The Flory–Huggins theory[1] has contributed substantially to the understanding of concentrated polymer solutions. Besides providing quantitative formulas for thermodynamic predictions, it has given us insight into the statistical origins of the various free-energy terms. In the present work we employ a lattice model to provide an understanding of the molecular considerations which give rise to interfacial free energy and determine the average arrangement of polymer molecules at interfaces.

The model we shall adopt has its origins in the interfacial cell theories of Ono[2] and Ono and Kondo,[3] developed for the analysis of small molecule systems. Ash, Everett, and Findenegg[4] considered molecules which could occupy several cells. An extension to polymers presented by Roe[5] has been discussed elsewhere.[6]

This paper continues a series of contributions[6–8] aimed at developing and applying a general theory of inhomogeneous polymer systems. In some of the works the continuous Gaussian random walk model has been used for the statistics of polymer conformations. Applications have been made to block copolymers,[7] to the polymer–polymer[7] and polymer solution–solvent[8] interfaces. The Gaussian random walk statistics should be appropriate when the scale of the inhomogeneity is large compared with the length of a polymer segment. For the interface problem "scale of inhomogeneity" refers to some measure of the region of significant phase mixing. It is difficult to say a priori how useful the Gaussian model will be for narrower interfaces. An alternative approach is the use of lattice statistics. One application of the lattice model already reported[6] is to the polymer–polymer interface problem. In the present paper these ideas are extended to the description of interfaces involving concentrated solutions.[9]

Our exposition begins with a specification of the lattice model. The major theoretical development is the derivation of a formula for the system's entropy. The entropy is combined with a random contact heat of mixing expression, and the resulting free energy is minimized, subject to appropriate constraints, to produce formulas for the systems' features. One of these constraints, which we call the "flux constraint", is unfamiliar, so it is discussed extensively in section V.

Numerical solutions of the equations, together with a qualitative discussion of phenomena, are presented in the following paper.[10] There, too, one finds a brief summary of the major features of this paper.

There is a strong parallel between the present work and our earlier lattice theory of polymer–polymer interfaces. We have tried to make this report reasonably self-contained, but some material is presented in greater detail in ref 6, although minor adaptions are necessary.

I. The Model

We will consider that n_P polymer units and n_o solvent molecules fill a lattice of n sites:

$$n = n_o + n_P \qquad (I.1)$$

The lattice is regarded as consisting of layers labeled with the index l. Each layer contains n_S cells.

There are two types of problems: either we have an interphase between a saturated polymer solution and solvent, in which case we allow l to run from $-\infty$ (solvent) to $+\infty$ (polymer solution); or we have in mind that there is an impenetrable wall, whereupon we let l go from 1 to ∞. The theories are so similar we present them simultaneously.

Each cell of the lattice has z nearest neighbors. If there is a polymer unit in a cell, the next unit along the chain can be in any of the z neighboring cells. (We will not take account of bond-angle restrictions or weighting of rotational states, although it could be done, as indicated in ref 6.)

For treatments of an inhomogeneity in the l direction it is necessary to specify that, of the z neighbors, a fraction m are in the layer above, a fraction m are below, and a fraction $(1 - 2m)$ are in the same layer.

The polymer molecules will be taken as being of extremely high molecular weight so that all units of the polymer will be regarded as middle segments. Some of the factors of importance if the molecular weight were finite have been alluded to in ref 6 and 7.

For purposes of calculating the entropy we will arbitrarily assign names to the polymer units and solvent molecules in the following manner. If the degree of polymerization is Z (a large number) label the units of one of the macromolecules $k = 1$ to Z. Then label $(n_o/n_P)Z$ (or the nearest integral number) solvent molecules with $k = Z + 1$ to $Z + (n_o/n_P)Z$. Proceed in this alternate fashion so that to within order (Z/k) the ratio of labeled polymer units to solvent is n_o/n_P at any k. The state of the system can be specified by indicating the cells $\mathcal{R} \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$ in which polymer units and solvent molecules $1, 2, \ldots, n$ are located. Though Flory and Huggins derive their results by first adding all the polymer and then the solvent, for a homogeneous system the formula can be derived by adding units in any order, as will be seen below.

II. Entropy

Our fundamental task in calculating a useful approximate entropy will be to obtain an estimate for the probability $P(\mathcal{R})$ of a state $\mathcal{R}$. There are some evident limitations on allowed states $\mathcal{R}$. The first is that given the cell, $\mathbf{r}_{k-1}$, occupied by a polymer unit $k - 1$, $\mathbf{r}_k$ must be one of the z neighboring cells. The second is that two units, polymer or solvent, may not occupy the same cell. The latter condition makes the stochastic process of filling the lattice non-Markoffian. Subsequently we will handle this prohibition against double occupancy in a mean-field manner, in the fashion of Flory and Huggins.

Let us temporarily remove the restriction against double occupancy, and call the probability of a state in that case $P^{(0)}(\mathcal{R})$. In ref 6 we have argued that as a mean-field approximation we may regard the process of filling the lattice as Markoffian. By this we mean that the conditional probability $p(\mathbf{r}_k|\mathcal{R}_{k-1};k)$ that a unit k goes into cell $\mathbf{r}_k$ given that the earlier units went into cells $\mathcal{R}_{k-1} \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{k-1}$ depends only on the cell that $k - 1$ is in:

$$p(\mathbf{r}_k|\mathcal{R}_{k-1};k) = p(\mathbf{r}_k|\mathbf{r}_{k-1};k) \qquad \text{(II.1)}$$

The influences of all units besides k and $k - 1$ are treated in a mean sense. In that case we can write $P^{(0)}$ as

$$P^{(0)}(\mathcal{R}) = \prod_{k=1}^{n} p(\mathbf{r}_k|\mathbf{r}_{k-1};k) \qquad \text{(II.2)}$$

Let us consider that k refers to a polymer unit. In keeping with our assumption that the degree of polymerization is large, let k be a unit not near a chain end. When the system is uniform, all cells neighboring $\mathbf{r}_{k-1}$ are equally likely for unit k so

$$p^{\text{homog}}(\mathbf{r}_k|\mathbf{r}_{k-1};k) = 1/z \qquad \text{(II.3)}$$

Under inhomogeneous conditions $p(\mathbf{r}_k|\mathbf{r}_{k-1};k)$ is a function of the level l of cell $\mathbf{r}_{k-1}$. It also depends on a variable ν which tells whether the layer index of $\mathbf{r}_k$ is greater than, the same as, or less than the layer index of $\mathbf{r}_{k-1}$:

$$\nu = \begin{Bmatrix} + \\ 0 \\ - \end{Bmatrix} \overset{\text{if the}}{(\text{layer of } \mathbf{r}_k) - (\text{layer of } \mathbf{r}_{k-1})} = \begin{Bmatrix} +1 \\ 0 \\ -1 \end{Bmatrix} \qquad \text{(II.4)}$$

Thus, in the inhomogeneous case, we should introduce an anisotropy factor, and write

$$p(\mathbf{r}_k|\mathbf{r}_{k-1};k) \equiv g_l^{\nu}/z \qquad \text{(II.5)}$$

A g_l^{ν} greater than unity indicates a greater than random chance for a bond with one end on the level l to go to a cell in the ν direction. How to make g_l^{ν} compatible with a given density distribution, and how to calculate it will be the subject of section IV.

In the following discussion we will need the joint probability $p(\mathbf{r}_k,\mathbf{r}_{k-1};k)$ of polymer units $k - 1$ and k being in $\mathbf{r}_{k-1}$ and $\mathbf{r}_k$, respectively. The joint and conditional probabilities are related by

$$p(\mathbf{r}_k,\mathbf{r}_{k-1};k) = p(\mathbf{r}_k|\mathbf{r}_{k-1};k)p(\mathbf{r}_{k-1};k-1) \qquad \text{(II.6)}$$

Here $p(\mathbf{r}_k;k)$ is the probability that unit k is in cell $\mathbf{r}_k$. When k is a polymer unit

$$p(\mathbf{r}_k;k) = \varphi_{l\text{P}}/n_\text{P} \qquad \text{(II.7)}$$

where $\varphi_{l\text{P}}$ is the volume fraction of polymer in layer l.

When k refers to a solvent molecule, there is no correlation with molecule $k - 1$ so

$$p(\mathbf{r}_k|\mathbf{r}_{k-1};k) = p(\mathbf{r}_k;k) \qquad \text{(II.8)}$$

$$= \varphi_{lo}/n_o \qquad \text{(II.9)}$$

where φ_{lo} is the volume fraction of solvent in layer l. Note that the explicit k variable in the p's serves only to tell us whether the unit is polymer or solvent.

To restore the restriction against multiple cell occupany we can write

$$P(\mathcal{R}) = P^{(0)}(\mathcal{R})\,\Lambda(\mathcal{R})/\Psi \qquad \text{(II.10)}$$

where $\Lambda(\mathcal{R})$ is a factor which equals unity if $\mathcal{R}$ has no multiple occupancies and zero otherwise. Since $\Lambda(\mathcal{R})$ eliminates many states, the probability P must be renormalized to unity, which is the role of Ψ.

A physical significance can be attached to Ψ by noting that

$$\Psi = \sum_{\mathcal{R}} P^{(0)}(\mathcal{R})\Lambda(\mathcal{R}) \qquad \text{(II.11)}$$

is the fraction of all states $\mathcal{R}$ which have no overlaps. Following Flory and Huggins we obtain a mean-field estimate of Ψ. Consider a sequential filling of the lattice with units $1, 2, \ldots, n$, in that order. Because the procedure of alternate addition keeps the composition essentially constant, the lattice is filled homogeneously. An estimate of the probability that the $(k + 1)$st unit will enter a cell not previously occupied is $[1 - (k/n)]$. This may be termed a mean-field estimate in that it neglects correlations. [Most seriously, when k is polymer it neglects the correlation with the $(k - 1)$st unit. This type of correlation is a form of bond angle condition (prohibition of 180° bond angle) and can be treated in a more detailed theory by introducing higher order correlation functions.] Using the uncorrelated estimate we obtain for Ψ, which is the probability of no overlap on every step,

$$\Psi = \prod_{k=0}^{n-1}\left[1 - \frac{k}{n}\right] \qquad \text{(II.12)}$$

$$\sim e^{-n} \qquad \text{(II.13)}$$

As can be seen, no reference has been made to the order of addition of polymer and solvent.

The object of the discussion, to this point, has been to enable us to write a formula for the entropy in terms of a few simple functions, viz., the φ's and g's, for which formulas will be obtained by minimizing the free energy. In general the entropy is

$$S = -k_\text{B}\,\Sigma P(\mathcal{R}) \log P(\mathcal{R}) - k_\text{B} \log (N_\text{P}!n_o!) - k_\text{B}N_\text{P} \log 2 \qquad \text{(II.14)}$$

where k_B is Boltzmann's constant, and $N_\text{P} = n_\text{P}/Z$ is the number of polymer molecules. The last two terms of eq

II.14 account for symmetry with respect to interchange of molecules and end-to-end inversion of the polymer molecules. Substituting the explicit form, eq II.10, for $P(\mathscr{R})$ we find

$$S = k_{\mathrm{B}} \log \Psi - \frac{k_{\mathrm{B}}}{\Psi} \sum_{\mathscr{R}} P^{(0)}(\mathscr{R}) \Lambda(\mathscr{R}) \log P^{(0)}(\mathscr{R}) - k_{\mathrm{B}} \log (N_{\mathrm{P}}! n_{\mathrm{o}}!) - k_{\mathrm{B}} N_{\mathrm{P}} \log 2 \quad \text{(II.15)}$$

We now assume that of all states which have a probability $P^{(0)}(\mathscr{R}) = P'$ a fraction Ψ have no multiple occupancy, independent of P'. This assumption is in keeping with the mean-field estimate of Ψ.[4] The summation in eq II.15 can then be extended to all states, rather than being restricted to nonoverlapping states by the factor $\Lambda(\mathscr{R})$, but the restricted sum is Ψ times the unrestricted sum

$$\frac{1}{\Psi} \sum_{\mathscr{R}} P^{(0)}(\mathscr{R}) \Lambda(\mathscr{R}) \log P^{(0)}(\mathscr{R}) = \int \mathrm{d}P' P' \log P' \frac{1}{\Psi} \sum_{\mathscr{R}} \Lambda(\mathscr{R}) \delta[P^{(0)}(\mathscr{R}) - P'] \approx \int \mathrm{d}P' P' \log P' \sum_{\mathscr{R}} \delta[P^{(0)}(\mathscr{R}) - P'] = \sum_{\mathscr{R}} P^{(0)}(\mathscr{R}) \log P^{(0)}(\mathscr{R}) \quad \text{(II.16)}$$

Next insert the mean-field (Markoffian) approximation for $P^{(0)}(\mathscr{R})$

$$P^{(0)}(\mathscr{R}) = \prod_{k \,\epsilon\, \text{solv}} p(\mathbf{r}_k;k) \prod_{k \,\epsilon\, \text{polym}} p(\mathbf{r}_k | \mathbf{r}_{k-1};k) \quad \text{(II.17)}$$

and by substituting eq II.5 to II.9 we find

$$S = k_{\mathrm{B}} n_{\mathrm{P}} \log (z/e) + \Delta S^{\mathrm{mix}} \quad \text{(II.18)}$$

$$\Delta S_{\mathrm{mix}} = -k_{\mathrm{B}} n_{\mathrm{S}} \sum_l \{\varphi_{l\mathrm{o}} \log \varphi_{l\mathrm{o}} + \varphi_{l\mathrm{P}} [m g_l^+ \log g_l^+ + (1 - 2m) g_l^{\mathrm{o}} \log g_l^{\mathrm{o}} + \mathrm{m g_l}^- \log g_l^-]\} + 0(1/Z) \quad \text{(II.19)}$$

The intermediate steps needed to get from eq II.15 to II.19 are similar to the steps taken to get from eq III.17 to III.25 in ref 6 and presented in greater detail there. The terms inversely proportional to the degree of polymerization, arising from translation freedom of polymer molecules and end corrections to conformational statistics, will be disregarded because of the high degree of polymerization assumed.

The entropy of mixing has been correctly identified in eq II.18 since $k_{\mathrm{B}} n_{\mathrm{P}} \log (z/e)$ is the entropy of pure polymer. The entropy of pure solvent is zero in this model because internal degrees of freedom have been disregarded all along.

III. Heat and Free Energy of Mixing, and Interfacial Tension

The heat of mixing for a polymer–solvent system against an inpenetrable wall will be taken in random mixing form,[1] modified for inhomogeneity:

$$\Delta H_{\mathrm{mix}} = \chi k_{\mathrm{B}} T n_{\mathrm{S}} \sum_l \varphi_{l\mathrm{P}} [\varphi_{l\mathrm{o}} + m(\varphi_{l+1,\mathrm{o}} - 2\varphi_{l\mathrm{o}} + \varphi_{l-1,\mathrm{o}})] + k_{\mathrm{B}} T n_{\mathrm{S}} m (\chi_{\mathrm{P}} \varphi_{1\mathrm{P}} + \chi_{\mathrm{o}} \varphi_{1\mathrm{o}}) \quad \text{(III.1)}$$

where T is temperature. When a wall is present the l sum goes from 1 to ∞. The last term allows for specific interactions between the wall and the units in the first layer. This will contribute to specific adsorptions. On the other hand, if we are considering the interphase between a solvent and a polymer solution we omit the final term and let l vary from $-\infty$ to $+\infty$.

In use, we may allow $\chi k_{\mathrm{B}} T$ to be temperature dependent, in which case eq III.1 represents not a heat but a free energy (called contact or interchange free energy).

The total free energy of mixing is

$$\Delta F_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T \Delta S_{\mathrm{mix}} \quad \text{(III.2)}$$

For a variety of purposes we will need expressions for the chemical potential of the polymer and solvent. These we will take as being of the form given by the Flory–Huggins theory[1]

$$\Delta\mu_{\mathrm{o}}/k_{\mathrm{B}}T = \chi(\varphi_{\mathrm{P}}^*)^2 + \log \varphi_{\mathrm{o}}^* + \varphi_{\mathrm{P}}^* \quad \text{(III.3)}$$

$$\Delta\mu_{\mathrm{P}}/k_{\mathrm{B}}T = \chi(\varphi_{\mathrm{o}}^*)^2 - \varphi_{\mathrm{o}}^* \quad \text{(III.4)}$$

where φ_{o}^* and $\varphi_{\mathrm{P}}^* = 1 - \varphi_{\mathrm{o}}^*$ are the volume fractions of solvent and polymer in the solution phase. Equations III.3 and III.4 are compatible with the above formula for the free energy of mixing.

In the case of a solution–solvent interface the chemical potential of solvent must be the same in both phases. Since one phase is pure solvent, the bulk concentration of solvent is determined by

$$0 = \Delta\mu_{\mathrm{o}}/k_{\mathrm{B}}T = \chi(1 - \varphi_{\mathrm{o}}^*)^2 + \log \varphi_{\mathrm{o}}^* + (1 - \varphi_{\mathrm{o}}^*) \quad \text{(III.5)}$$

For the polymer solution against a wall φ_{o}^* is an independent parameter which may be varied from zero to the saturation value given by eq III.5.

The surface tension is defined by subtracting from the total free energy the free energy of the molecules in uniform phases

$$\gamma n_{\mathrm{S}} a = \Delta F^{\mathrm{mix}} - n_{\mathrm{o}} \Delta\mu_{\mathrm{o}} - n_{\mathrm{P}} \Delta\mu_{\mathrm{P}} \quad \text{(III.6)}$$

where a is the cross-sectional area of a cell. (Since ΔpV on mixing is zero for a lattice model, pressure–volume terms and the difference between Helmholtz and Gibbs free energy do not concern us.)

IV. Equations for the Concentration Profile and Anisotropy Factors

Equations for the concentrations $\varphi_{l\mathrm{o}}$ and $\varphi_{l\mathrm{P}}$, as well as for the anisotropy factors g_l^{ν}, may be obtained by minimizing the free energy with respect to these variables. However, the unknowns are not all independent because they are subject to a number of constraints. The fixed numbers of polymer units and solvent molecules are related to the volume fractions by

$$n_{\mathrm{P}} = n_{\mathrm{S}} \sum_l \varphi_{l\mathrm{P}} \quad \text{(IV.1)}$$

$$n_{\mathrm{o}} = n_{\mathrm{S}} \sum_l \varphi_{l\mathrm{o}} \quad \text{(IV.2)}$$

Complete occupancy requires that

$$\varphi_{l\mathrm{P}} + \varphi_{l\mathrm{o}} = 1 \quad \text{(IV.3)}$$

The normalization of the anisotropy factors is

$$m g_l^+ + (1 - 2m) g_l^0 + m g_l^- = 1 \quad \text{(IV.4)}$$

Finally, there is a relation between the φ's and g's which we call the flux constraint:

$$\varphi_{l\mathrm{P}} g_l^+ = \varphi_{l+1,\mathrm{P}} g_{l+1}^- \quad \text{(IV.5)}$$

This ensures that the number of bonds going up from layer l equals the number coming down from $l + 1$, as demanded by symmetry. Further aspects of the flux constraint are discussed in the following section.

The constraints are introduced with Lagrange multipliers: $\Delta\mu_P$ for eq IV.1 (we immediately use the explicit form for this Lagrange multiplier, which from Grand Canonical Ensemble theory is known to be a chemical potential), $\Delta\mu_o$ for eq IV.2, $k_BTn_Sw_l^\zeta$ for eq IV.3, $k_BTn_S\varphi_{lP}(\xi_l - 1)$ for eq IV.4, and $k_BTn_Sm\lambda_l$ for eq IV.5. The new variables are w_l^ζ, ξ_l, and λ_l; the other factors are introduced for convenience. The function to be minimized is

$$\frac{\Delta F_{\text{mix}}}{k_BTn_S} = \Big(\sum_l \chi\{\varphi_{lP}[\varphi_{lo} + m(\varphi_{l+1,o} - 2\varphi_{lo} + \varphi_{l-1,o})] - \varphi_{lP}(\varphi_o^*)^2 - \varphi_{lo}(\varphi_P^*)^2\} + \varphi_{lo}\log(\varphi_{lo}/\varphi_o^*) - \varphi_{lo}\varphi_P^* + \varphi_{lP}\varphi_o^* + w_l^\zeta(\varphi_{lP} + \varphi_{lo} - 1) + \varphi_{lP}[mg_l^+(\log g_l^+ + \xi_l - 1 + \lambda_l) + (1 - 2m)g_l^o(\log g_l^o + \xi_l - 1) + mg_l^-(\log g_l^- + \xi_l - 1 - \lambda_{l-1}) - \xi_l + 1]\Big) + m(\chi_P\varphi_{1P} + \chi_o\varphi_{1o}) + \frac{n_P\Delta\mu_P + n_o\Delta\mu_o}{n_Sk_BT} \quad \text{(IV.6)}$$

The result of the minimization is

$$g_l^0 = \exp(-\xi_l) \quad \text{(IV.7)}$$

$$g_l^+ = \exp(-\xi_l - \lambda_l) \quad \text{(IV.8)}$$

$$g_l^- = \exp(-\xi_l + \lambda_{l-1}) \quad \text{(IV.9)}$$

$$\exp(\xi_l) = 1 + m[\exp(-\lambda_l) - 2 + \exp(\lambda_{l-1})] \quad \text{(IV.10)}$$

$$\exp(-2\lambda_l) = \frac{\varphi_{l+1,P}}{\varphi_{lP}}\exp(\xi_l - \xi_{l+1}) \quad \text{(IV.11)}$$

$$-\xi_l + 2\chi[\varphi_{lo} - \varphi_o^*] + 2m\chi(\varphi_{l+1,o} - 2\varphi_{lo} + \varphi_{l-1,o}) - \log(\varphi_{lo}/\varphi_o^*) + m(\chi_P - \chi_o)\delta_{l1} = 0 \quad \text{(IV.12)}$$

Solutions of this set of difference equations will be presented in the following paper.[10]

Using eq IV.7 to IV.9 in eq III.6 and IV.6, one obtains an explicit form for the surface tension

$$\frac{\gamma a}{k_BT} = \sum_l [-(1 - \varphi_{lo})\xi_l - \chi(\varphi_{lo} - \varphi_o^*)^2 + \chi m(1 - \varphi_{lo})(\varphi_{l+1,o} - 2\varphi_{lo} + \varphi_{l-1,o}) + \varphi_{lo}\log(\varphi_{lo}/\varphi_o^*) - (\varphi_{lo} - \varphi_o^*)] + [m(\chi_P - \chi_o)(1 - \varphi_{1o}) + m\chi_o] \quad \text{(IV.13)}$$

The summand directly vanishes for l deep into the solution, and it also vanishes for l in the solvent phase (if present) when eq III.5 is used.

V. The Flux Constraint

In this section we will examine several facets of the flux constraint, eq IV.5, relating the anisotropy factors to the concentrations.

When we stated above that the flux constraint followed by symmetry we were referring to the following argument. For every conformation $\mathcal{R}$ there is another one of equal probability in which the units of each polymer molecule are inserted in reverse order: 1 goes into $\mathbf{r}_Z$, 2 into $\mathbf{r}_{Z-1}$, etc. In general, if the index k refers to a polymer molecule with indices $k' + 1$ to $k' + Z$, then unit $k' + 1$ would go into $\mathbf{r}_{k'+Z}$, . . ., unit $k' + Z - k + k' + 1$ would go into $\mathbf{r}_k$, unit $k' + Z - k + k' + 2$ would go into $\mathbf{r}_{k-1}$, etc. Therefore,

$$p(\mathbf{r}_k,\mathbf{r}_{k-1};k) = p(\mathbf{r}_{k-1},\mathbf{r}_k,k' + Z - k + k' + 2) \quad \text{(V.1)}$$

The k dependencies are unimportant for k not near a chain end, so the flux constraint follows from

$$p(\mathbf{r}_k,\mathbf{r}_{k-1};k) = \frac{1}{n_P}\varphi_{lP}\frac{1}{z}g_l^\nu \quad \text{(V.2)}$$

where l is the layer of $\mathbf{r}_{k-1}$ and ν is the direction from the layers of $\mathbf{r}_{k-1}$ to $\mathbf{r}_k$.

Now let us look at the flux constraint in another manner, which will also motivate the name. An equation of continuity is

$$p(\mathbf{r}_k;k) - p(\mathbf{r}_k;k - 1) = \sum_{r_{k-1}} p(\mathbf{r}_k,\mathbf{r}_{k-1};k) - p(\mathbf{r}_k;k - 1) \quad \text{(V.3)}$$

The first term on the right represents the probability of entering cell $\mathbf{r}_k$ at stage k, while the second term is the probability of leaving $\mathbf{r}_k$ at stage k. The left-hand side of the equation is zero by virtue of the stationarity of the stochastic process; or, more fundamentally, because of the identity of the units when end effects are neglected. Another form of eq V.3 is

$$0 = mg_{l-1}^+\varphi_{l-1,P} + (1 - 2m)g_l^o\varphi_{lP} + mg_{l+1}^-\varphi_{l+1,P} - \varphi_{lP} \quad \text{(V.4)}$$

or in terms of "fluxes"

$$0 = -j_l + j_{l-1} \quad \text{(V.5)}$$

where

$$j_l \equiv m(g_l^+\varphi_{lP} - g_{l+1}^-\varphi_{l+1,P}) \quad \text{(V.6)}$$

is the "flux" from layer l to $l + 1$. Equation V.6 says that the flux is a constant, but since the flux vanishes at ±∞ the constant is zero, and the flux constraint follows.

A greater appreciation of the flux constraint, and of other aspects of this theory, will be gained when one sees in the next paper the types of interfacial effects which are induced.

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