

Stability and phase separation in mixed self-assembled monolayers

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Recent single molecule experiments rely on the self-assembly of binary mixtures of molecules with very different properties in a stable monolayer, in order to probe the characteristics of the interspersed molecule of interest in a controlled environment. However, not all efforts at coassembly have been successful. To study systematically the behavior of such systems, we derive the free energy of multicomponent systems of rods with configurational degrees of freedom, localized on a surface, starting from a generalized van der Waals description. The molecular parameters are determined by geometrical factors of the molecules and by their pairwise van der Waals interactions computed using molecular mechanics. Applying the model to two experimental situations, we are able to use the stability analysis of the respective mixtures to explain why coassembly was successful in one set of experiments (carotene and alkanethiol) and not in another (benzenethiols and alkanethiol). We outline general guidelines for suitable choices of molecules to achieve coassembly. © 2006 American Institute of Physics. [DOI: [10.1063/1.2336198](https://doi.org/10.1063/1.2336198)]

I. INTRODUCTION

With the development of scanning probe microscopy and of self-assembly methods for preparing both three-dimensional structures and monolayer films, modern chemical science is paying increasing attention to planar nanostructures. Widely applied synthetic schemes include organosilane-based films on hydroxylated surfaces and those based on the use of thiol/coinage metal Lewis pairing to provide self-assembled monolayers (SAMs) of organothiols on a metallic host. This has been extended to include semiconductor supports. These assemblies are used very broadly, in areas as different as biological isolation and molecular electronics.^{1–23} Indeed, a recent single number of a major chemistry journal²⁴ contains four papers using mixed SAMs for various applications.

The assembly mechanisms at the back of these self-assembled monolayers, and their general characteristics and phase behavior, are critical for understanding how their structure/function properties arise. One of the simplest questions is coassembly: this centers on the two-component phase diagram, when two differing adspecies, such as differ-

ing organic thiols, are assembled on a single substrate. These have been studied quite extensively, particularly in the area of molecular electronics, where a more conductive structure (almost always an unsaturated organothiol) is placed in an inert host structure, which is usually a stable alkanethiol. Extensive experimentation has been based on such mixtures, and the nature of the sequestering of the host within the guest structure has been addressed, particularly in the context of grain boundaries and the effects of underlying surface defects.²¹

Here we examine the more general problem of coassembly in a model for two-component molecular structures on a given surface. We utilize a mean-field theory to evaluate the phase diagram. Specific attention is paid to equilibrium aspects of coassembly, and the general behaviors of the phase boundary regions are predicted. We use molecular modeling techniques to deduce the important parameters characterizing the potentials, which we assume to be dominated by space filling and van der Waals interactions. For particular cases, the simple model is capable of predicting limits of the coexistence region, in which stable coassembly is expected.

In Sec. II we use the free energy derived in the Appendix to determine the thermodynamic stability of binary mixtures

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TABLE I. The definition and numerical values (where applicable) of all symbols used in the text.

Variable/parameter	Definition	Benzenethiol/alkanethiol	Carotene/alkanethiol
f	(Helmholtz) free energy per unit area		
β	$1/k_B T$		
N	Total number of molecules		
V	Total area		
ρ	Number density= N/V		
$b_{\nu,\xi}$	Excluded volume between rods of type ν and ξ		
$A_{\nu,\xi}$	van der Waals parameter between rods of types ν and ξ		
$A_{\alpha\alpha}$ (kcal/mol)		-5.01	-11.78
$A_{\gamma\gamma}$ (kcal/mol)		-15.98	-15.98
$A_{\alpha\gamma}$ (kcal/mol)		-3.07	-4.14
x	Mole fraction of species $\alpha=N_\alpha/N$		
r	Length (l) to width (w) ratio of rods	2	3
ϕ	Tilt angle of species γ	20°	20°
\bar{h} (kcal/mol)	Adsorption energy difference between species α and γ	2	2

of SAMs for experimentally relevant systems.^{25,26} Section III presents representative calculations for the model systems. In Sec. IV we discuss our results and their implications for the formation of mixed monolayers. In particular, we explain why (experimentally) coassembly was observed in one case and not in another.

II. APPLICATION: TWO-COMPONENT SYSTEM WITH FIXED ORIENTATIONS

A number of theoretical approaches have been developed to address issues similar to those involved in discussing SAM structures.^{27–37} The generalized van der Waals theory, originally formulated by Longuet-Higgins and Widom²⁷ and Kac *et al.*²⁸ and applied to simple liquids, provides a systematic way to elucidate the role of competing interactions in the phase behavior of molecular systems. It rests on the main assumptions that at short range the intermolecular repulsions of the system are satisfactorily described by hard-core exclusions, while the long-range attractive interactions provide a “mean field” under which a particular particle or molecule moves. A generalization of those equations²⁹ to apply to more complex systems such as grafted rods has been useful in the classification of phase transitions in single component rod monolayers.^{30,31}

Previous work has been concerned with the classification of phase transitions, the nature of the order parameter, and the role of internal degrees of freedom such as the orientational angle. The qualitative main result is that a first order phase transition is possible only in the presence of attractions.³²

The previous analysis was only concerned with single component monolayers. Here, we are interested in the effect on the chemical stability and phase behavior brought about by competing interactions between different species. The advantage of the free energy obtained in the Appendix is that it is expressed using molecular interaction parameters yet through an analytical formalism. For a two-component system of molecules α and γ , with composition of species

$\tilde{s}_\alpha=x$ ($\tilde{s}_\gamma=1-x$) and where each species assumes a preferred orientation, the free energy per unit area f [Eq. (A3)] is reduced to

$$\begin{aligned} \beta f = & \rho \ln \rho + \rho [x \ln x + (1-x) \ln(1-x)] + \rho \beta (\tilde{h}x + h_\gamma) \\ & - \rho \ln \left[1 - \frac{\rho}{2} (x^2 b_{\alpha\alpha} + (1-x)^2 b_{\gamma\gamma} + x(1-x) \right. \\ & \times (b_{\alpha\gamma} + b_{\gamma\alpha})) \left. \right] + \beta \frac{\rho^2}{2} [x^2 A_{\alpha\alpha} + (1-x)^2 A_{\gamma\gamma} \\ & + 2x(1-x)(A_{\alpha\gamma})], \end{aligned} \quad (1)$$

where the density $\rho=N/V$ is given by the total number of molecules N on a surface of total area V . $\beta=1/kT$; the b 's correspond to the volume, and the A 's to the attractions between species; the h_α and h_γ are surface binding energies, $\tilde{h} \equiv h_\alpha - h_\gamma$ (see also Table I and the Appendix).

The first two terms in Eq. (1) correspond to the entropy of mixing, the third term describes surface binding, while the term in the second line is the excluded volume repulsion term. Finally, the last term corresponds to the attraction between rods. The symbols are defined in Table I.

From the general conditions for stable equilibrium on the Helmholtz free energy (constant area) for multicomponent systems derived by Gibbs,³³ we can obtain the stability curve for our system. The general stability criterion, namely,

$$\delta^2 F = \frac{1}{2} \sum_{\nu,\xi} \frac{\partial^2 F}{\partial N_\nu \partial N_\xi} \delta N_\nu \delta N_\xi > 0, \quad \nu, \xi = \alpha, \gamma,$$

requires that the matrix M with entries

$$M_{\nu\xi} = \frac{\partial^2 F}{\partial N_\nu \partial N_\xi}$$

be positive definite, so that the equality (the spinodal) marks the onset of stability of the system.

The phase behavior of a mixture described by the free energy presented in Eq. (1) includes gas-liquid coexistence, in which each phase has, in general, a different density and a different composition, and liquid-liquid coexistence, in which the two liquid phases are composed of different mole

fractions of each species. Therefore, there are two lines of critical points that describe the onset of phase transitions. The solution of the full phase diagram is relevant when the energy of adsorption of the two species is relatively small. In that case the number of molecules adsorbed is dependent on the thermodynamic conditions of the solution in contact with the surface. The rich phase behavior obtained in this case is not relevant for the type of experimental observations that we are trying to explain. However, the presentation of the general theory is done for its future implementation in related self-assembled systems.

In the experimental SAMs that we are studying it is safe to assume that the overall density of molecules on the surface is fixed and determined by a strong binding energy. Therefore, the density is not a thermodynamic relevant variable because it is fixed. However, the composition on the surface is to be determined by the thermodynamic equilibrium state. The onset of stability is given by the spinodal, which for fixed density, is given by

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_{T,\rho} = 0. \quad (2)$$

The relevant thermodynamic quantity at constant density is the exchange chemical potential μ (henceforth called chemical potential) which is given by

$$\mu = \left(\frac{\partial f}{\partial x}\right)_{\rho,T},$$

and the spinodal points occur at the extrema of the chemical potential curve.

Furthermore, at the critical point,

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_{T,\rho} = \left(\frac{\partial^3 f}{\partial x^3}\right)_{T,\rho} = 0 \text{ and } \left(\frac{\partial^4 f}{\partial x^4}\right)_{T,\rho} > 0. \quad (3)$$

At coexistence, the chemical potential and the relevant pressure, $\Pi v = x\mu - f$ (where $v = \rho^{-1}$), must be equal in each phase. Namely,

$$\mu(x_I) = \mu(x_{II}), \quad \Pi(x_I) = \Pi(x_{II}). \quad (4)$$

Again, note that we have a pseudo-one-component system since the density is fixed, i.e., the only relevant thermodynamic composition variable is x , and thus we have two equations to determine the two compositions at coexistence.

From Eq. (1) then we obtain the derivatives after substituting for

$$\bar{B} \equiv 1/2[x^2 b_{\alpha\alpha} + (1-x)^2 b_{\gamma\gamma} + x(1-x)(b_{\alpha\gamma} + b_{\gamma\alpha})]$$

and

$$\bar{A} \equiv 1/2[x^2 A_{\alpha\alpha} + (1-x)^2 A_{\gamma\gamma} + 2x(1-x)A_{\alpha\gamma}].$$

The chemical potential is

$$\begin{aligned} \beta\mu = \beta\left(\frac{\partial f}{\partial x}\right)_{T,\rho} &= \rho \ln[x/(1-x)] + \rho\beta\bar{h} + \frac{\rho^2\bar{B}'}{1-\rho\bar{B}} \\ &+ \beta\rho^2\bar{A}'. \end{aligned} \quad (5)$$

The pressure is given by

$$\begin{aligned} \beta\Pi = \rho^2 \left[-\beta h_\gamma - \beta\rho\bar{A} + \ln\left[\frac{(1-\rho\bar{B})}{(1-x)\rho}\right] + \beta x\rho\bar{A}' \right. \\ \left. + x\frac{\rho\bar{B}'}{(1-\rho\bar{B})} \right]. \end{aligned} \quad (6)$$

To determine the critical point we need the following two explicit derivatives:

$$\begin{aligned} \beta\left(\frac{\partial^2 f}{\partial x^2}\right)_{T,\rho} &= \frac{\rho}{[x(1-x)]} + \frac{\rho^2\bar{B}''}{1-\rho\bar{B}} + \frac{\rho^3(\bar{B}')^2}{(1-\rho\bar{B})^2} \\ &+ \beta\rho^2(A_{\alpha\alpha} + A_{\gamma\gamma} - 2A_{\alpha\gamma}), \end{aligned} \quad (7)$$

$$\beta\left(\frac{\partial^3 f}{\partial x^3}\right)_{T,\rho} = \rho\frac{2x-1}{x^2(1-x)^2} + \frac{3\rho^3\bar{B}''\bar{B}'}{(1-\rho\bar{B})^2} + \frac{2\rho^4(\bar{B}')^3}{(1-\rho\bar{B})^3}, \quad (8)$$

where “'” denotes the derivative with respect to x .

From Eqs. (3) and (8) we obtain the critical composition x_{crit} , and substituting in Eq. (7) gives the critical temperature T_{crit} . Solving Eqs. (7) and (2) for T gives the spinodal equation. Namely, the maximum and minimum of the chemical potential provide the two compositions, at temperature below the critical point, that represent the onset of metastability. Finally, solving the coupled equations in (4), with the explicit expressions (5) and (6), we obtain the coexistence curve or binodal, i.e., the onset of thermodynamic stability.

A. Evaluating the molecular parameters

To proceed we need to obtain the specific parameters for the system of interest. The van der Waals interaction parameter corresponds to

$$A_{\nu,\xi} = \int_{\sigma}^{\infty} u_{\text{att},\nu,\xi}(r) 2\pi r dr, \quad \nu, \xi = \alpha, \gamma, \quad (9)$$

which is the two dimensional analog of the usual a van der Waals (vdW) parameter, with σ denoting the intermolecular distance between nearest neighbor molecules ν and ξ at the given density ρ . The molecular information that enters the theory is included in the determination of the intermolecular attractive potential $u_{\text{att},\nu,\xi}(r)$ and of the intermolecular excluded volume presented below. We determine the intermolecular attractive interactions using molecular mechanics with the UFF force field.³⁴ For each type of molecular pair we perform the following steps: (i) optimize the structure of each molecule (monomer), (ii) obtain the full intermolecular potential at the given assumed angle between the molecules, and (iii) use the attractive part of the potential to obtain the integral in Eq. (9). The obtained vdW parameter is then used in the thermodynamic expressions derived above. The explicit results for the molecular mixtures studied here are presented in Table I.

To compute the excluded volume terms we need to specify the geometry of the rods. The simplest case, approximating the molecules by parallelepipeds, originally introduced by Zwanzig,³⁵ has been proven useful in predicting behaviors of grafted rods and liquid crystals. We adopt it

here and use r to denote the ratio of length l to width w ($r=l/w$) as a measure of the anisotropy of the molecule. It is possible to consider in the future more complex shapes for the molecule³⁶ or include polarization effects.³⁷ Furthermore, the inclusion will disrupt the molecular order in the monolayer, as the two molecules may have preferentially different anchoring angles. Hence, there will be a tilting angle among the molecules of different types. Taking this into account, the excluded volume values between a molecule α (assuming that it binds preferentially perpendicular to the surface) and a molecule γ (that tilts at an angle ϕ) then are given by

$$b_{\alpha\alpha} = 2w^2,$$

$$b_{\gamma\gamma} = w^2(1/\cos \phi + \cos \phi + r \sin \phi),$$

$$b_{\alpha\gamma} = w^2(1 + \cos \phi + r \sin \phi),$$

$$b_{\gamma\alpha} = w^2(1 + 1/\cos \phi + r \sin \phi)$$

from purely geometrical arguments.

We turn now to systems for which experimental data are available. In particular, we consider first the molecules of Ref. 25, namely, the insertion of 4-(2'-ethyl-4'-(phenylethylene)phenylthiolate (molecule α ; we will refer to it as benzenethiol) into a dodecane thiolate (molecule γ) monolayer on a Au(111) substrate. Subsequently, we apply the model to the molecules of Ref. 26 where the extended conjugated structure is a carotenoid thiol (molecule α) inserted in the monolayer of molecules γ as in the previous example. While SAMs of n -alkane systems chemisorbed on Au(111) have been the most widely studied, ordered SAMs of conjugated molecules of the type of molecule α have been successfully formed.^{7,38} The benzenethiols appear as standing, with a tilt of 10° , while the alkanes (molecules γ) tilt by 30° . Hence, the angle ϕ is chosen to be $\phi = 20^\circ$. Also, nearest neighbors are 5.2 \AA apart for molecule α (Ref. 38) and 4.99 \AA for molecule γ .³ With the above information we can compute the attractive interactions³⁹ which are reported in Table I. The structure in the monolayers also allows us to approximate $r=2$. The length of the molecules is 20 \AA for the benzenethiols and 15 \AA for the dodecane thiolates, and they occupy a projected surface area of 50 \AA^2 on the average, which also constitutes the unit of area w^2 in our calculations.

Finally, the adsorption energy is mainly determined by the terminal bond. It is reported that the bond of species γ is considerably stronger than molecule α (twice).^{25,38} So we take the energy of adsorption to be twice as much. In the second example we consider, molecule α is now carotene. However, molecule γ remains the same, so most of the geometrical factors are retained, except for the ratio of length to width ($r=3$).

III. RESULTS

The phase diagram in the space of composition, temperature, and density may be obtained, as discussed in Sec. II. However, while the composition of the mixture may be controlled, that is not the case for the density. The SAMs of

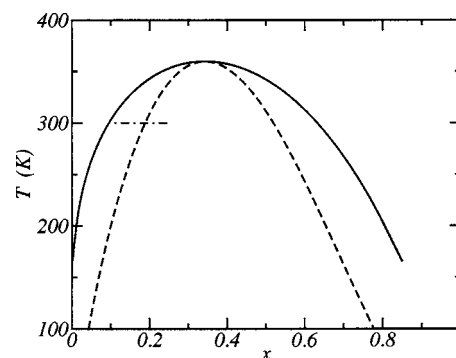


FIG. 1. Spinodal (dashed curve) and binodal (solid curve) curves for benzenethiol-dodecanethiol mixture plotted against the concentration x of the benzenethiol. The experiment is at room temperature and in the composition range $x \in [0.11, 0.25]$ (Ref. 25), shown as the horizontal line.

interest here form high density ordered structures. The typical value of area per molecule is near 50 \AA^2 , which corresponds to unity of our density in reduced units. Room temperature is also another typical experimental condition. In Fig. 1, we plot the binodal and spinodal at unit density for the system of Ref. 25, namely, of benzenethiol and dodecanethiol. The area under the spinodal curve corresponds to the unstable part of the system. The region between the spinodal and binodal corresponds to the range of temperature and composition in which the film is metastable. The experimental compositions for the insertion molecule reported ranged from $x=0.11$ to 0.25 .²⁵ This is marked by the horizontal line in the figure. We can see that this range of compositions corresponds to the unstable region of the phase diagram for half of the range and the metastable region for the other half. Therefore, one would expect that in most cases no coassembly will be achieved. To find the system outside the spinodal at these compositions and temperature, higher density is required (results not shown) that is probably outside the experimentally relevant range for the thiols. However, lowering the concentration of the benzenethiols would place the system outside the unstable regions. It is important to emphasize that even in the metastable region one expects the formation of the SAMs to be in domains. The expected very slow translations of the molecules on the surface, which would lead to macroscopic phase separation, are therefore not observed, and the result is no coassembly at all the experimental studied compositions.²⁵

The same analysis is applied to the system of Ref. 26. It is now a carotenoid-alkanethiol mixture. From the binodal and spinodal curves of Fig. 2 we can see that the system is usually in unstable regions for the experimental temperature and density. However, the reported compositions of the mixture are substantially smaller (for example, 0.003 and 0.015 for carotene). Hence the system is in the stable (at most metastable) region, as marked by a circle in the figure.

IV. DISCUSSION AND CONCLUSIONS

A generalized van der Waals theory has been applied to the thermodynamic behavior of mixed self-assembled monolayers. In particular, we considered two examples from the experimental literature, one where coassembly was not

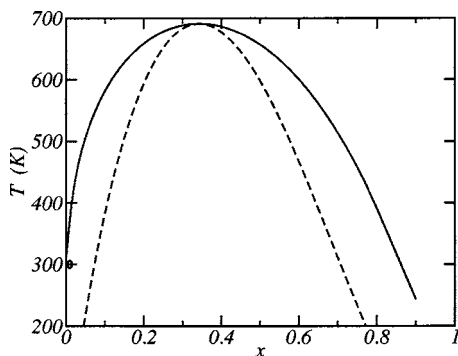


FIG. 2. Spinodal (dashed line) and binodal (solid line) curves for carotene-dodecanethiol mixture plotted against the concentration x of the carotene. The experiment is at room temperature and in the composition range $x \in [0.003, 0.015]$, marked by a circle.

achieved and one where it was successful. Coassembly corresponds to the formation of stable unsegregated monolayers containing both species after cochemisorption from the same solution. By using the molecular parameters corresponding to the systems of interest, namely, the molecular area and tilt as well as the van der Waals attractions, we find that we can explain the difference in behavior by examining the stability of the phase diagram within a mean-field treatment. Specifically, the two experiments correspond to different points in the phase diagram. One case falls in an unstable region for the mixture, while the other is stable. As a general trend, we find that, assuming that room temperature is a necessary experimental condition, lower concentration for the inclusion of bulkier molecules or lower density monolayers will help the system to find itself in the stability region.

There are several ways to extend this work and pursue more detailed questions. Site dependent adsorption energy including preferential binding to step edges or terraces as well as the role of defects may be incorporated in the formalism and may be worth exploring, as it is known that properties of SAMs are dependent on surface morphology. The adsorption energy term of Eq. (A2) can be modified to explicitly take into account these effects.

The theory presented here is a simple approach in which explicit molecular information is incorporated into a mean-field framework. This approach enables the determination of the phase behavior of the mixed SAM systems, and one can explore large regions of phase space. The results from the theory can be used as starting points for more sophisticated computational methods, such as atomistic computer simulations, which are computationally too expensive to use for many different conditions. Furthermore, the theory can serve as the starting point for the experimental design of mixed layers with desired mixing behavior.

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APPENDIX: GENERALIZED VAN DER WAALS FORMULATION: DERIVATION OF THE HELMHOLTZ FREE ENERGY FUNCTIONAL

We consider the most general k -component mixture, each component ν consisting of N_ν rigid chains of different stiffnesses on a surface of total area V . The total number of chains is N such that

$$\sum_{\nu=1}^k N_\nu = N, \quad \nu = \alpha, \gamma, \dots, \quad (\text{A1})$$

and the density $\rho = N/V$. The classical configuration partition function Q_N is given by

$$Q_N = \frac{1}{\prod N_\nu!} \int d\Omega^N \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N, \Omega^N)],$$

where $\beta = 1/k_B T$ and Ω denotes the configurational degrees of freedom. The interaction potential U of the rod mixture contains three essential terms: the adsorption energy for each chain, the attractive interactions among chains, and the excluded volume (repulsive) terms. Hence, it may be expressed by

$$U(\mathbf{r}^N, \Omega^N) = \sum_{\nu, i} h_{\nu, i}(\mathbf{r}_i^N, \Omega_i^N) + \sum_{\nu, \nu' \langle i, j \rangle} U_{\nu, \nu'}^{\text{attr}}(\mathbf{r}_{ij}, \Omega_i, \Omega_j) + \sum_{\nu, \nu' \langle i, j \rangle} U_{\nu, \nu'}^*(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = V^{\text{ads}} + V^{\text{attr}} + V^*,$$

where the sums i and j run over all rods and $\langle \rangle$ denotes nearest neighbor interactions.

We consider a discrete number of orientations n , so for each species ν , $N_{\nu, \sigma}$ ($\sigma = 1, \dots, n$) molecules have orientation Ω_σ . By dividing the total solid angle into n such sections $\Delta\omega (n = 4\pi/\Delta\omega)$, Q_N becomes

$$Q_N = \frac{1}{\prod N_\nu! (4\pi)^N} \sum_{\nu} \dots \sum_{N_{k,n}} \frac{\Delta\omega^N \prod N_\nu!}{\prod N_{\nu, \sigma}!} \int d\mathbf{r}^N \exp(-\beta U).$$

Next, we invoke the largest term approximation: in the thermodynamic limit, $\ln Q \rightarrow \ln Q(\tilde{N}_\Omega)$, that is, the maximal term in the sum (the most probable or equilibrium configuration) denoted by \tilde{N}_Ω approximates the total. So,

$$Q_N \approx \frac{(\Delta\omega)^N}{(4\pi)^N \prod N_{\nu, \sigma}!} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N, \tilde{N}_\Omega)].$$

At this stage, we perform the mean-field approximation, that is, replace the attractive terms by their average value,

$$\tilde{V}^{\text{attr}} \sim (1/2)V^{-1} \sum_{\nu, \sigma} \sum_{\nu', \sigma'} \tilde{N}_{\nu, \sigma} \tilde{N}_{\nu', \sigma'} \times \int d\mathbf{r} U_{\nu, \nu'}^{\text{attr}}(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}) g(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}),$$

where g is the pair correlation function of molecules of orientation Ω_σ and $\Omega_{\sigma'}$ at distance \mathbf{r} . We will later assume that this is determined solely by the rod's excluded volume.

If we also consider that all sites are equivalent, that is, that there are no defects or steps on the surface, the adsorption energy does not depend on position either:

$$Q_N = \frac{(\Delta\omega)^N}{(4\pi)^N} \prod_{\nu,\sigma} \frac{e^{-\beta\tilde{N}_{\nu,\sigma}(\Omega_\sigma)}}{\tilde{N}_{\nu,\sigma}!} \exp(-\beta\bar{V}^{\text{attr}}) \\ \times \int d\mathbf{r}^N \exp(-\beta V^*(\mathbf{r}, \tilde{N}_\Omega)).$$

To obtain the configurational Helmholtz free energy per unit area, f , then,

$$\beta f \equiv \beta F/V = (-\rho/N) \ln Q_N = \rho \ln(4\pi\rho/\Delta\omega) \\ + \rho \sum_{\nu,\sigma} \tilde{s}_{\nu,\sigma} \ln \tilde{s}_{\nu,\sigma} + \beta\rho \sum_{\nu,\sigma} \tilde{s}_{\nu,\sigma} h_\nu(\Omega_\sigma) \\ + (1/2)\beta\rho^2 \sum_{\nu,\sigma} \sum_{\nu',\sigma'} \tilde{s}_{\nu,\sigma} \tilde{s}_{\nu',\sigma'} \\ \times \int d\mathbf{r} U_{\nu,\nu'}^{\text{attr}}(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}) g(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}) \\ - (1/V) \ln \left[(1/V)^N \int d\mathbf{r}^N \exp(-\beta V^*(\mathbf{r}, \tilde{N}_\Omega)) \right], \quad (\text{A2})$$

where $\tilde{s}_{\nu,\sigma} = \tilde{N}_{\nu,\sigma}/N_\nu$ is the mole fraction of each species ν in orientation Ω_σ . The first term in Eq. (A2) corresponds to the translational entropy of the chains, and the second describes the orientational as well as the entropy of mixing (for chains of different species). The subsequent term corresponds to the adsorption energy $h_\nu(\Omega_\sigma)$ for species ν with orientation Ω_σ in the presence of a surface and may include any other one-body potentials appropriate to a specific system. The last two terms are the pair interaction approximations to the many-body attractive and repulsive potentials respectively.

If we assume that the pair correlation function is unity when chains do not overlap and zero otherwise and use the following definitions for the excluded volume terms:

$$b_{\nu,\nu'}^{\sigma,\sigma'} = \int d\mathbf{r} g^{\nu,\nu'}(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}),$$

and similarly for the attractive interaction terms,

$$A_{\nu,\nu'}^{\sigma,\sigma'} = \int d\mathbf{r} U_{\nu,\nu'}^{\text{attr}}(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}) g^{\nu,\nu'}(\mathbf{r}, \Omega_\sigma, \Omega_{\sigma'}),$$

Eq. (A2) becomes⁴⁰

$$\beta f = \rho \ln(4\pi\rho/\Delta\omega) + \rho \sum_{\nu,\sigma} \tilde{s}_{\nu,\sigma} \ln \tilde{s}_{\nu,\sigma} + \beta\rho \sum_{\nu,\sigma} \tilde{s}_{\nu,\sigma} h_\nu(\Omega_\sigma) \\ + (1/2)\beta\rho^2 \sum_{\nu,\sigma} \sum_{\nu',\sigma'} \tilde{s}_{\nu,\sigma} \tilde{s}_{\nu',\sigma'} A_{\nu,\nu'}^{\sigma,\sigma'} \\ - \rho \ln \left[1 - (\rho/2) \sum_{\nu,\sigma} \sum_{\nu',\sigma'} \tilde{s}_{\nu,\sigma} \tilde{s}_{\nu',\sigma'} b_{\nu,\nu'}^{\sigma,\sigma'} \right]. \quad (\text{A3})$$

The parameters $b_{\nu,\nu'}^{\sigma,\sigma'}$ and $A_{\nu,\nu'}^{\sigma,\sigma'}$ are fixed by the choice of molecular species: the former by the geometrical shape of the molecules, as will be shown in detail in Sec. II A, and the

latter by their van der Waals interactions that may be computed by molecular mechanics, for example. The energy of adsorption may be estimated from experimental results.

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