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Theory of Surface Ordering on Solutions of Rigid-Rod-Like Molecules

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ABSTRACT: This paper discusses the surface ordering and the adsorption phenomena of solutions of rigid-rod-like molecules. Here we focus on the planar adsorption of the rigid-rod-like molecules. We find that, for the attractive wall which preferentially adsorbs the rodlike molecules, the surface phase has two phase transitions when the bulk concentration is increased: One transition occurs when the adsorption amount jumps at a concentration ϕ_c where the surface phase changes from an isotropic to a nematic state while the bulk is still in an isotropic state. The other occurs when the adsorption isotherms have a kink at the bulk critical concentration ϕ_{IN} where the bulk phase changes from an isotropic to a nematic state. For the bulk concentration $\phi_c < \phi < \phi_{IN}$, we find the wetting of an isotropic bulk phase with a nematic surface phase. When $\phi < \phi_c$ ($\phi > \phi_{IN}$), both bulk and the surface phases are in isotropic (nematic) states. For various values of the axial ratio of the rigid-rod-like molecules and adsorption energy, we examine the adsorption isotherms, the surface tensions, and the surface phase transitions. We also discuss the surface transitions on repulsive walls.

1. Introduction

Adsorption phenomena of polymer on a surface play an important role for many practical important processes such as colloidal particle stabilization, wetting, and adhesion. For these reasons, polymer adsorption on a surface has been of theoretical and experimental interest. The main attention, however, has been paid to the adsorption of flexible polymer chains. Here we focus on the surface properties on the solutions of rigid-rod-like molecules, including liquid crystals and liquid crystalline polymers. Such properties are also important to applications in displays.

It is well-known that a solution of rigid-rod-like molecules shows a transition from an isotropic to a nematic phase and the transition is of the first order.[1–5] This behavior is induced by the excluded-volume interaction between the molecules, or the concentration. When the rigid-rod-like molecules are adsorbed to the surface from a bulk solution, the surface phase may also take a ordered state depending on the adsorption amounts, or surface concentration. The adsorption energy considered here is the order of thermal energy, so that the adsorbed molecules can change their own orientation on the surface phase.[6] Then we can easily expect the surface-nematic behavior when the adsorption amount is increased. Surface ordering behaviors depending on the temperature have been studied for thermotropic liquid crystals from both theoretical[7–9] and experimental[10] points of view.

In this paper we study the surface ordering behavior on the solutions of rigid-rod-like molecules. Here we focus on planar adsorption of the rigid-rod-like molecules. There are some types of configurations of adsorbed molecules,[11] such as homeotropic or planar, depending on the interactions between the molecule and the wall (surface).[12] The orientation-dependent excluded-volume interaction between the rigid-rod-like molecule and the wall favors the planar alignment of the molecules,[13] and so it is useful to first consider planer adsorption on a surface. We here ignore the effects of the flexibility[14] of the molecules. On the basis of the Flory theory of the rigid-rod-like particles,[3] we examine the molecular orientations in both bulk and the surface phases and we calculate the adsorption amounts, the surface tension, and the degree of surface ordering as a function of the adsorption energy, the axial ratio of the rigid-rod-like molecules, and the bulk concentration.

From the simple discussions, we see that the surface of solutions of rigid-rod-like molecules has some phase transitions. We here consider the attractive wall which corresponds to preferential rodlike molecule adsorption. In this case, the surface phase is more ordered than the bulk phase because of the adsorption amounts ϕ_s is larger than the bulk concentration ϕ. At the extremely dilute solutions, both the bulk and the surface phases are in isotropic states. When the bulk concentration increases, the surface changes from an isotropic to a nematic state at a bulk concentration ϕ_c. With a further increase of the concentration, the isotropic–nematic transition (INT) in the bulk phase takes place at the bulk concentration ϕ_{IN}. For the concentration $\phi_c < \phi < \phi_{IN}$, we can expect that the bulk is in an isotropic state and the surface is in a nematic state. At $\phi > \phi_{IN}$, both the surface and the bulk phases are in nematic states. We then see that the nematic surface phase is formed on the top of the isotropic bulk phase at $\phi_c < \phi < \phi_{IN}$. For the repulsive wall which corresponds to preferential solvent adsorption ($\phi > \phi_s$), when the bulk concentration ϕ is increased, the bulk phase becomes a nematic state at ϕ_{IN}. With further increasing ϕ, the surface is ordered at the bulk concentration ϕ_c. For the concentration $\phi_{IN} < \phi < \phi_c$, the isotropic surface phase is formed on the top of the nematic bulk phase.[12] Thus we can expect that the surface of the solutions of rigid-rod-like molecules has some phase regions.

To examine the above qualitative results, we introduce our model at the following sections. We predict the wetting of the isotropic bulk phase with a nematic surface phase and the wetting of the nematic bulk phase with more ordered nematic surface phase.

2. Lattice Model of Surface Thermodynamics

Consider a binary mixture of rigid-rod-like molecules and solvent near a surface. The surface can be either

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an attractive or a repulsive wall. There are some types of configurations of adsorbed molecules, such as homeotropic or planar, depending on the interactions between the molecule and the wall (surface). We here study the planar adsorption of rigid-rod-like molecules to a surface. We assume that the thickness of the surface corresponds to one lattice site, and only the first layer of the solution has a different composition from the bulk. Hereafter we refer to the layer as the surface phase. The adsorption energy considered here is on the order of thermal energy, so that the molecules can change the sites on the surface phase. The surface phase corresponds to a two-dimensional solution with all rodlike molecules in contact with the surface. Then the surface and the bulk phases can be described by the Flory lattice theory of hard rods.[3] These assumptions have been used in the surface thermodynamics of polymer solutions.[15,16]

We first consider the free energy of a bulk phase. Let N_0 be the number of solvent molecules and N be the number of rigid-rod-like molecules whose axial ratio is x. The total lattice site of the bulk phase is given by $N_t = N_0 + xN$. The volume of the bulk phase is given by $V = a^3N_t$, where a^3 is the volume of a unit lattice. According to Flory theory,[3] the free energy of mixing for the bulk phase is given by

$$\beta\Delta F_{\mathrm{mix}}{}^{\mathrm{b}} = N_t\Big[(1-\phi)\ln(1-\phi) + \frac{\phi}{x}\ln\phi - \Big[1-\Big(1-\frac{y}{x}\Big)\phi\Big]\ln\Big[1-\Big(1-\frac{y}{x}\Big)\phi\Big] - \frac{\phi}{x}[\ln(xy^2) - y + 1] + \chi\phi(1-\phi)\Big] \qquad (2.1)$$

where $\beta \equiv 1/(k_BT)$, k_B is the Boltzmann constant and T the absolute temperature, $\phi = xN/N_t$ is the bulk volume fraction of the rodlike molecules, and $k_BT\chi$ is the energy change per segment on transferring a solute molecule from the pure solute to the infinite solution. When a rigid-rod-like molecule of axial ratio x orients at an angle θ to the domain axis of the bulk phase, the disorder parameter y is defined by $y = x \sin\theta$.

Similarly, the free energy of mixing for the surface phase is given by

$$\beta\Delta F_{\mathrm{mix}}{}^{\mathrm{s}} = N_t{}^{\mathrm{s}}\Big[(1-\phi_s)\ln(1-\phi_s) + \frac{\phi_s}{x}\ln\phi_s - \Big[1-\Big(1-\frac{y_s}{x}\Big)\phi_s\Big]\ln\Big[1-\Big(1-\frac{y_s}{x}\Big)\phi_s\Big] - \frac{\phi_s}{x}[\ln(xy_s{}^2) - y_s + 1] - a^2\beta\gamma\Big] \qquad (2.2)$$

where $\phi_s = xN^s/N_t{}^s$ is the surface volume fraction of the rodlike molecules, γ is the surface tension, and y_s is the disorder parameter of the surface. This assumes that the rods of the bulk molecules do not penetrate to the surface layer. At the thermal equilibrium, the values of y and y_s can be determined from the condition of minimization of the free energy (2.1) and (2.2) with respect to y and y_s, respectively:

$$\exp(-2/y) = 1 - \phi(1 - y/x) \qquad (2.3)$$

$$\exp(-2/y_s) = 1 - \phi_s(1 - y_s/x) \qquad (2.4)$$

where y is the disorder parameter which characterizes the average orientation of the rodlike molecules in the bulk phase and y_s that on the surface phase.

Substituting $y = x$ into eq 2.1, we obtain the free energy for the isotropic bulk phase:

$$\beta\Delta F_{\mathrm{mix,I}}{}^{\mathrm{b}} = N_t{}^{\mathrm{b}}\Big[(1-\phi)\ln(1-\phi) + \frac{\phi}{x}\ln\phi - \frac{\phi}{x}[3\ln x - x + 1] + \chi\phi(1-\phi)\Big] \qquad (2.5)$$

and substituting $y_s = x$ into eq 2.2, we obtain the free energy for the isotropic surface phase:

$$\beta\Delta F_{\mathrm{mix,I}}{}^{\mathrm{s}} = N_t{}^{\mathrm{s}}\Big[(1-\phi_s)\ln(1-\phi_s) + \frac{\phi_s}{x}\ln\phi_s - \frac{\phi_s}{x}[3\ln x - x + 1] - a^2\beta\gamma\Big] \qquad (2.6)$$

From the definition, the chemical potentials of the nematic bulk phase are given by $\Delta\mu_{0,N} = (\partial\Delta F_{\mathrm{mix}}{}^{\mathrm{b}}/\partial N_0)_{T,N}$ for the solvent (component 0) and by $\Delta\mu_{1,N} = (\partial\Delta F_{\mathrm{mix}}{}^{\mathrm{b}}/\partial N)_{T,N_0}$ for the solute (component 1). From eqs 2.1 and 2.3 we obtain

$$\beta(\mu_{0,N}{}^{\mathrm{b}} - \mu_{0,N}{}^{\circ}) = \ln(1-\phi) + \frac{2}{y} + \frac{\phi}{x}(y-1) + \chi\phi^2 \qquad (2.7)$$

$$\beta(\mu_{1,N}{}^{\mathrm{b}} - \mu_{1,N}{}^{\circ}) = \ln(\phi/x) + 2(1 - \ln y) + \phi(y-1) + x\chi(1-\phi)^2 \qquad (2.8)$$

where $\mu_{0,N}{}^{\circ}$ ($\mu_{1,N}{}^{\circ}$) is the chemical potential of a pure solvent (solute) in a nematic phase. Similarly from eq 2.5 the chemical potentials of the isotropic bulk phase are given by

$$\beta(\mu_{0,I}{}^{\mathrm{b}} - \mu_{0,I}{}^{\circ}) = \ln(1-\phi) + (1 - 1/x)\phi + \chi\phi^2 \qquad (2.9)$$

$$\beta(\mu_{1,I}{}^{\mathrm{b}} - \mu_{1,I}{}^{\circ}) = \ln(\phi/x) + \phi(x-1) - 2\ln x + x\chi(1-\phi)^2 \qquad (2.10)$$

where $\mu_{0,I}{}^{\circ}$ ($\mu_{1,I}{}^{\circ}$) is the chemical potential of a pure solvent (solute) in an isotropic phase. From eq 2.6 with eq 2.4 we further derive the chemical potentials of the nematic surface phase and of the isotropic surface phase as follows:

$$\beta\mu_{0,N}{}^{\mathrm{s}} = \beta\mu_{0,N}{}^{\circ,\mathrm{s}} + \ln(1-\phi_s) + 2/y_s + \phi_s(y_s - 1)/x - \beta a^2\gamma \qquad (2.11)$$

$$\beta\mu_{1,N}{}^{\mathrm{s}} = \beta\mu_{1,N}{}^{\circ,\mathrm{s}} + \ln(\phi_s/x) + 2(1 - \ln y_s) + \phi_s(y_s - 1) - x\beta a^2\gamma \qquad (2.12)$$

$$\beta\mu_{0,I}{}^{\mathrm{s}} = \beta\mu_{0,I}{}^{\circ,\mathrm{s}} + \ln(1-\phi_s) + (1 - 1/x)\phi_s - \beta a^2\gamma \qquad (2.13)$$

$$\beta\mu_{1,I}{}^{\mathrm{s}} = \beta\mu_{1,I}{}^{\circ,\mathrm{s}} + \ln(\phi_s/x) + \phi_s(x-1) - 2\ln x - x\beta a^2\gamma \qquad (2.14)$$

When the bulk phase of a pure solvent is in an isotropic state or the bulk phase of a pure solute is in a nematic state, we can rewrite $\mu_{0,N}{}^{\circ}$ and $\mu_{1,I}{}^{\circ}$ as $\mu_{0,I}{}^{\circ}$ and $\mu_{1,N}{}^{\circ}$, respectively. For the same reasons, the chemical potentials $\mu_{0,N}{}^{\circ,\mathrm{s}}$ and $\mu_{1,I}{}^{\circ,\mathrm{s}}$ of pure components in the surface phase can also be rewritten as $\mu_{0,\mathrm{I}}{}^{\circ,\mathrm{s}}$ and $\mu_{1,\mathrm{N}}{}^{\circ,\mathrm{s}}$, respectively.

3. Adsorption Isotherm of Rodlike Molecular Solutions

In the attractive wall corresponding to preferential solute adsorption ($\phi_\mathrm{s} > \phi$), we have three surface regions depending on the bulk concentration. At extremely dilute solutions, or where the adsorption amount ϕ_s is very low, both the bulk and surface phases are in isotropic states. As the bulk concentration ϕ is increased, the adsorption amount ϕ_s increases and the surface phase changes from an isotropic to a nematic state at a bulk concentration ϕ_c while the bulk phase is still in an isotropic state. The rigid-rod-like molecules are oriented at an angle to the domain axis on the surface phase. Further increasing bulk concentration ϕ, the bulk phase changes from an isotropic to a nematic state at the bulk critical concentration ϕ_IN. Then at $\phi > \phi_\mathrm{IN}$, both the bulk and surface phases are in the nematic state.

In thermal equilibrium, the chemical potentials in bulk and the surface are equated. We then have the thermal equilibrium condition

$$\mu_{0,\mathrm{I}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{0,\mathrm{I}}{}^{\mathrm{b}}(\phi) \quad (3.1)$$

$$\mu_{1,\mathrm{I}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{1,\mathrm{I}}{}^{\mathrm{b}}(\phi) \quad (3.2)$$

for dilute solution $\phi < \phi_\mathrm{c}$ (region (I,I)), where both bulk and the surface are in isotropic states,

$$\mu_{0,\mathrm{N}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{0,\mathrm{I}}{}^{\mathrm{b}}(\phi) \quad (3.3)$$

$$\mu_{1,\mathrm{N}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{1,\mathrm{I}}{}^{\mathrm{b}}(\phi) \quad (3.4)$$

for intermediate concentration $\phi_\mathrm{c} < \phi < \phi_\mathrm{IN}$ (region (N,I)), where the surface is in a nematic state while bulk is in an isotropic state, and

$$\mu_{0,\mathrm{N}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{0,\mathrm{N}}{}^{\mathrm{b}}(\phi) \quad (3.5)$$

$$\mu_{1,\mathrm{N}}{}^{\mathrm{s}}(\phi_\mathrm{s}) = \mu_{1,\mathrm{N}}{}^{\mathrm{b}}(\phi) \quad (3.6)$$

for $\phi > \phi_\mathrm{IN}$ (region N,N)), where both bulk and the surface are in nematic states.

Substituting eqs 2.9, 2.10, 2.13, and 2.14 into eqs 3.1 and 3.2, the surface tension in region (I,I) is given by

$$a^2\beta\gamma = a^2\beta\gamma_0 + \ln\frac{1-\phi_\mathrm{s}}{1-\phi} + (1 - 1/x)(\phi_\mathrm{s} - \phi) - \chi\phi^2 \quad (3.7)$$

$$a^2\beta\gamma = a^2\beta\gamma_1 + (1/x)\ln(\phi_\mathrm{s}/\phi) + (1 - 1/x)(\phi_\mathrm{s} - \phi) - \chi(1-\phi)^2 \quad (3.8)$$

where $\gamma_0 \equiv (\mu_{0,\mathrm{I}}{}^{\circ,\mathrm{s}} - \mu_{0,\mathrm{I}}{}^{\circ})/a^2$ is the surface tension of a pure solvent and $\gamma_1 \equiv (\mu_{1,\mathrm{N}}{}^{\circ,\mathrm{s}} - \mu_{1,\mathrm{N}}{}^{\circ})/a^2$ is that of a pure solute molecule. By subtraction, eqs 3.7 and 3.8 yield the composition ϕ_s of the surface phase in region (I,I):

$$\frac{1-\phi_\mathrm{s}}{1-\phi} = \left(\frac{\phi_\mathrm{s}}{\phi}\right)^{1/x} \exp[a^2\beta(\gamma_1 - \gamma_0)]\exp[\chi(2\phi - 1)] \quad (3.9)$$

This equation is in the same form as the adsorption isotherms for flexible chains.[16]

From eqs 3.3 and 3.4 we obtain the surface tension in region (N,I) as follows:

$$a^2\beta\gamma = a^2\beta\gamma_0 + \ln\frac{1-\phi_\mathrm{s}}{1-\phi} - (1 - 1/x)\phi + \frac{2}{y_\mathrm{s}} + \phi_\mathrm{s}(y_\mathrm{s} - 1)/x - \chi\phi^2 \quad (3.10)$$

$$a^2\beta\gamma = a^2\beta\gamma_1 + \frac{1}{x}\ln\frac{\phi_\mathrm{s}}{\phi} - (1 - 1/x)\phi + \phi_\mathrm{s}(y_\mathrm{s} - 1)/x + \frac{2}{x}\left(1 + \ln\frac{x}{y_\mathrm{s}}\right) - \chi(1-\phi)^2 \quad (3.11)$$

and the adsorption isotherm in region (N,I) is given by

$$\frac{1-\phi_\mathrm{s}}{1-\phi} = \left(\frac{\phi_\mathrm{s}}{\phi}\right)^{1/x}\left(\frac{x}{y_\mathrm{s}}\right)^{2/x} \exp[2(1/x - 1/y_\mathrm{s})] \exp[a^2\beta(\gamma_1 - \gamma_0)]\exp[\chi(2\phi - 1)] \quad (3.12)$$

where y_s is given as a function of ϕ_s from eq 2.4.

From eqs 3.5 and 3.6 we obtain the surface tension in region (N,N) as follows:

$$a^2\beta\gamma = a^2\beta\gamma_0 + \ln\frac{1-\phi_\mathrm{s}}{1-\phi} + 2\left(\frac{1}{y_\mathrm{s}} - \frac{1}{y}\right) + \frac{1}{x}[\phi_\mathrm{s}(y_\mathrm{s} - 1) - \phi(y - 1)] - \chi\phi^2 \quad (3.13)$$

$$a^2\beta\gamma = a^2\beta\gamma_1 + \frac{1}{x}\ln\frac{\phi_\mathrm{s}}{\phi} - \frac{2}{x}\ln\frac{y_\mathrm{s}}{y} + \frac{1}{x}[\phi_\mathrm{s}(y_\mathrm{s} - 1) - \phi(y - 1)] - \chi(1-\phi)^2 \quad (3.14)$$

and the adsorption isotherm for region (N,N) is given by

$$\frac{1-\phi_\mathrm{s}}{1-\phi} = \left(\frac{\phi_\mathrm{s}}{\phi}\right)^{1/x}\left(\frac{y}{y_\mathrm{s}}\right)^{2/x} \exp\left[2\left(\frac{1}{y} - \frac{1}{y_\mathrm{s}}\right)\right] \exp[a^2\beta(\gamma_1 - \gamma_0)]\exp[\chi(2\phi - 1)] \quad (3.15)$$

where y_s and y are given by eqs 2.3 and 2.4, respectively. In the appendix we give the results for the repulsive wall.

These equations permit evaluations of surface composition and surface tension. In the next section we present the numerical results.

4. Results and Discussion

In our numerical calculation, we have three parameters characterizing our system: x, the axial ratio of a rigid-rod-like molecule; $\delta\gamma \equiv a^2\beta(\gamma_1 - \gamma_0)$, the dimensionless adsorption energy which is given by the difference between the surface tension γ_1 for a pure solute and the surface tension γ_0 for a pure solvent; and χ, the solvent–solute interaction parameter. We have fixed $\chi = 0.1$ and $\delta\gamma = -0.1$ for a typical example.

Figure 1 shows the adsorption amount ϕ_s plotted against the bulk volume fraction ϕ for $x = 50$. The broken line shows the adsorption isotherm of a flexible polymer chain with the same length.[15] The adsorption amount of the flexible chains is continuously increased with increasing the bulk concentration. The adsorption isotherm of the rigid-rod-like molecules, however, has two phase transitions at bulk concentrations ϕ_c and ϕ_IN. Point A corresponds to the bulk concentration ϕ_c, where the first-order phase transition from an isotropic to a nematic state appears on the surface phase. The

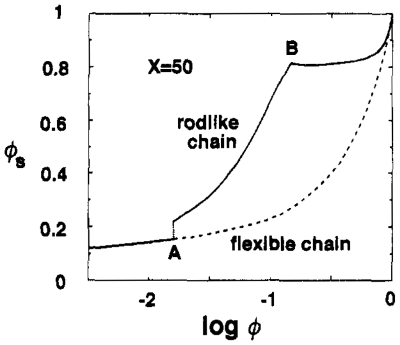

Figure 1. Adsorption isotherm of rigid-rod-like molecules for the attractive wall with $x = 50$, $\chi = 0.1$, and $\delta\gamma = -0.1$. The broken line shows the adsorption isotherm of a flexible chain with the same length. When the bulk concentration increases, the adsorption amount jumps at A(ϕ_c) where the surface phase changes from an isotropic to a nematic state. Further increasing ϕ, the adsorption isotherm has a kink at B(ϕ_{IN}) where the bulk phase changes from an isotropic to a nematic state.

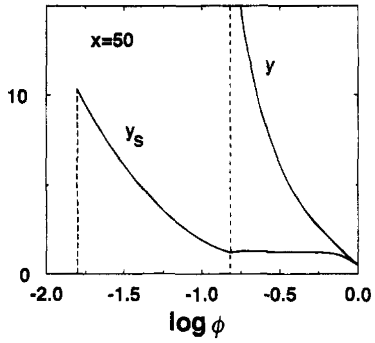

Figure 2. Disorder parameter y_s in surface and y in bulk are plotted as a function of log ϕ.

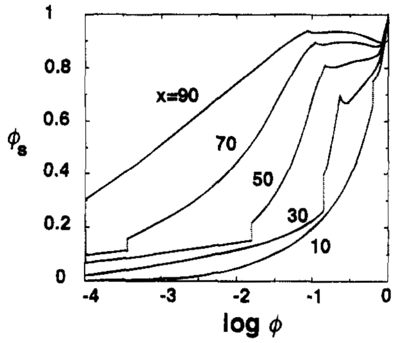

Figure 3. Adsorption isotherms for rigid-rod-like molecules of various lengths x.

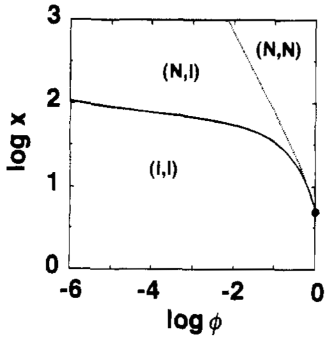

Figure 4. Isotropic–nematic transition curve of the bulk phase shown by the broken line, which is given by Flory.[3] The solid line corresponds to that of the surface phase.

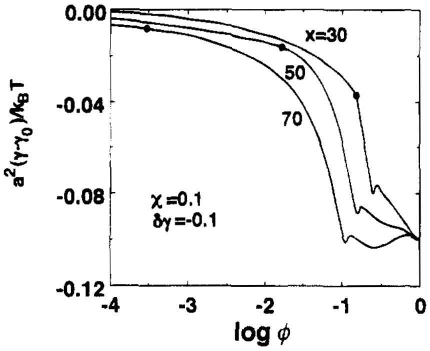

Figure 5. Surface tension as a function of log ϕ with various values of the axial ratio x.

adsorption amounts ϕ_s jump at the bulk volume fraction ϕ_c. Point B shows the bulk critical concentration ϕ_{IN}, where the bulk phase changes from an isotropic to a nematic state. The adsorption isotherm has a kink at ϕ_{IN}, and so the surface phase shows the second-order phase transition at the bulk critical concentration ϕ_{IN}. At $\phi > \phi_{IN}$, as shown in Figure 2, both the surface and the bulk phases are in nematic states. Near ϕ_{IN} desorption occurs in order to gain the bulk mixing entropy which is reduced by ordering of the bulk phase.

In Figure 2, the disorder parameter y in bulk and y_s in surface are shown against the bulk volume fraction ϕ. As the bulk concentration is increased, the disorder parameter y_s appears at ϕ_c where the isotropic–nematic transition (INT) occurs in the surface phase. The rodlike molecules on the surface are oriented at an angle θ_s to the domain axis on the surface. The value of y_s decreases with increasing the bulk concentration ϕ. From the relation $y_s = x \sin \theta_s$, the surface is gradually ordered as the concentration is increased. Further increasing the concentration, INT in the bulk phase occurs at ϕ_{IN} (point B), where the value of y_s has a kink as a function of the bulk volume fraction ϕ. The adsorption isotherm has a kink at ϕ_{IN} as shown in Figure 1. When $\phi < \phi_c$, both the bulk and surface phases are in isotropic states. When $\phi_c < \phi < \phi_{IN}$, the surface is in a nematic state while the bulk is in an isotropic state. When $\phi > \phi_{IN}$, both the bulk and surface phases are in nematic states and the surface is more ordered than the bulk phase. In Figure 3 we show the adsorption isotherms for various lengths x. As length x is increased, the critical concentration is shifted to a lower concentration. When $x = 30$, the adsorption isotherm has a sharp kink and a weak minimum near ϕ_{IN}. On increasing x, the kink becomes weak.

Figure 4 shows the three phase regions on the plane of the axial ratio x and the bulk volume fraction ϕ. The broken line shows the INT curve of the bulk phase,[3] and the solid line corresponds to the INT of the surface phase. The region (I,I) shows that both the surface and bulk phases are in isotropic states; (N,I), a nematic surface phase coexists with an isotropic bulk; (N,N), both surface and bulk phases are in nematic states.

Figure 5 shows the surface tension plotted against the bulk concentration ϕ for various values of x. The surface tension is decreased with increasing x. The closed circles show the surface tension at ϕ_c in which the curves bend. The corresponding adsorption isotherms are shown in Figure 3. In the region (N,N), the surface tension has a minimum and a maximum as a function of ϕ.

5. Conclusion

In this paper we have studied the adsorption of the rigid-rod-like molecules from solution. In Figure 6 we

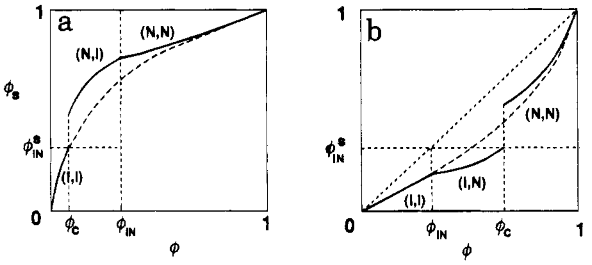

Figure 6. (a) Adsorption isotherm of solutions of a rigid-rod-like molecule for attractive walls. The isotropic–nematic transition in bulk and in the surface occurs at the critical concentration ϕ_c and ϕ_{IN}, respectively. The region (I,I) shows that both the surface and the bulk phases are in isotropic states, (N,I), that the surface is in a nematic state and the bulk is in an isotropic state, and (N,N), that both the surface and bulk phases are in nematic states. (b) Adsorption isotherm of solutions of a rigid-rod-like molecule for repulsive walls. The region (I,N) which shows the wetting of an nematic bulk with an isotropic surface appears at $\phi_{IN} < \phi < \phi_c$.

summarize the qualitative results of the adsorption isotherm of a rigid-rod-like molecule. Figure 6a shows some phase regions on the adsorption isotherm for the attractive wall ($\phi_s > \phi$). At extremely dilute solutions (I,I), both the surface and the bulk phases are in isotropic states. As the bulk concentration is increased, the surface concentration ϕ_s jumps at the bulk concentration ϕ_c where INT occurs in the surface phase. Further increasing the concentration, the adsorption isotherm has a kink at ϕ_{IN} where INT occurs in the bulk phase. Thus we have three regions (I,I), (N,I), and (N,N) as the bulk concentration is increased. The surface transition from (I,I) to (N,I) is of first order, and that from (N,I) to (N,N) is of second order. For the repulsive wall which corresponds to preferential solvent adsorption ($\phi > \phi_s$), we have the region (I,N) which shows the wetting of an nematic bulk with an isotropic surface. Figure 6b shows the adsorption isotherms at the repulsive wall. When the bulk concentration ϕ is increased, the adsorption isotherm has a kink at ϕ_{IN} where INT occurs in the bulk phase. With further increasing ϕ, the value of ϕ_s jumps at ϕ_c where INT occurs in the surface phase. For the bulk concentration $\phi_{IN} < \phi < \phi_c$, the isotropic surface phase is formed on the top of the nematic bulk phase. In conclusion, several types of surface-phase transitions will be obtained for the solutions of rigid-rod-like molecules with the first-order bulk transition.

Appendix: The Case of the Repulsive Wall ($\phi_s < \phi$)

We here consider the repulsive wall which corresponds to the preferential solvent adsorption ($\phi > \phi_s$). At extremely dilute solutions, both the bulk and surface phases are in isotropic states. In thermal equilibrium, the chemical potentials in bulk and the surface are equated. Then the condition is given by eqs 3.1 and 3.2. The surface tensions and the adsorption isotherms are given by eqs 3.7 and 3.9, respectively. As the bulk concentration is increased, the bulk phase changes from an isotropic to a nematic state at a bulk concentration ϕ_{IN}. Further increasing the concentration, the surface phase changes from an isotropic to a nematic state at a bulk concentration ϕ_c. When $\phi_{IN} < \phi < \phi_c$, the bulk phase is in a nematic state, while the surface is in an isotropic state. The thermal equilibrium condition is given by

$$\mu_{0,I}{}^{s}(\phi_s) = \mu_{0,N}{}^{b}(\phi) \qquad (A.1)$$

$$\mu_{1,I}{}^{s}(\phi_s) = \mu_{1,N}{}^{b}(\phi) \qquad (A.2)$$

Substituting eqs 2.7, 2.8, 2.13, and 2.14 into eqs A.1 and A.2, we obtain the surface tension:

$$a^2\beta\gamma = a^2\beta\gamma_0 + \ln\frac{1-\phi_s}{1-\phi} + (1-1/x)\phi_s - \frac{2}{y} - \phi(y-1)/x - \chi\phi^2 \qquad (A.3)$$

$$a^2\beta\gamma = a^2\beta\gamma_1 + \frac{1}{x}\ln\frac{\phi_s}{\phi} + (1-1/x)\phi - \phi(y-1)/x - \frac{2}{x}\left(1+\ln\frac{x}{y}\right) - \chi(1-\phi)^2 \qquad (A.4)$$

and the adsorption isotherm is given by subtraction of eqs A.3 and A.4 as follows:

$$\frac{1-\phi_s}{1-\phi} = \left(\frac{\phi_s}{\phi}\right)^{1/x}\left(\frac{y}{x}\right)^{2/x} \exp[2(1/y-1/x)] \exp[a^2\beta(\gamma_1-\gamma_0)] \exp[\chi(2\phi-1)] \qquad (A.5)$$

For $\phi > \phi_{IN}$, both the bulk and surface phases are in nematic states. The thermal equilibrium condition is given by eqs 3.5 and 3.6. The surface tensions and the adsorption isotherms are given by eqs 3.13 and 3.15, respectively.

References and Notes

(1) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
(2) Flory, P. J. *Proc. R. Soc. London* **1956**, *A234*, 60.
(3) Flory, P. J. *Proc. R. Soc. London* **1956**, *A234*, 73.
(4) Di Marzio, E. A. *J. Chem. Phys.* **1961**, *35*, 658.
(5) Odijk, T. *Macromolecules* **1986**, *19*, 2313.
(6) Rodriguez, A. L.; Wittman, H. P.; Binder, K. *Macromolecules* **1990**, *23*, 4327.
(7) Sheng, P. *Phys. Rev. Lett.* **1976**, *37*, 1059.
(8) Lipowsky, R.; Speth, W. *Phys. Rev.* **1983**, *B28*, 3983.
(9) Forgacs, G.; Lipowsky, R.; Nieuwenhuizen, Th. M. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic Press: New York, 1991; Vol. 14.
(10) (a) Immerschitt, S.; Koch, T.; Still, W.; Strobl, G. *J. Chem. Phys.* **1992**, *96*, 6249. (b) Beaglehole, D. *Mol. Cryst. Liq. Cryst.* **1982**, *89*, 319.
(11) Di Marzio, E. A. *J. Chem. Phys.* **1977**, *66*, 1160.
(12) (a) Kimura, H.; Nakano, H. *J. Phys. Soc. Jpn.* **1985**, *54*, 1730. (b) Kimura, H.; Nakano, H. *J. Phys. Soc. Jpn.* **1986**, *55*, 4186.
(13) Okano, K. *Jpn. J. Appl. Phys.* **1983**, *22*, L343.
(14) (a) Khokhlov, A. R.; Ternovsky, F. F. *Macromol. Chem. Theory Simul.* **1993**, *2*, 151. (b) Khokhlov, A. R.; Semenov, A. N. *Physica* **1981**, *108A*, 546.
(15) Gaines, G. L., Jr. *J. Phys. Chem.* **1969**, *73*, 3143.
(16) Siow, K. S.; Patterson, D. *J. Phys. Chem.* **1973**, *77*, 356.

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