

Competition between self-assembly and surface adsorption

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We investigate a minimal equilibrium polymerization model for the competition between self-assembly on a boundary and in solution that arises when an assembling system is in the presence of an adsorbing interface. Adsorption generally occurs upon cooling, but assembly (equilibrium polymerization) may arise either upon cooling or heating. Both cases are shown to exhibit a coupling between adsorption and self-assembly. When both assembly and adsorption proceed upon cooling, a change in the ratio of the enthalpy of adsorption to the enthalpy of assembly in solution can switch the system between a predominance of self-assembly in solution to assembly on the substrate. If assembly is promoted by heating and adsorption by cooling, as in many self-assembling proteins in aqueous solution, then a self-assembly analog of a closed loop phase boundary is found. In particular, the order parameter for assembly on the surface exhibits a peak as a function of temperature. As demonstrated by illustrative examples, the coupling between surface adsorption and self-assembly provides a powerful means of *switching* self-assembly processes on and off. Understanding and controlling this switching phenomenon will be useful in designing and directing self-assembly processes on surfaces for applications to nanomanufacturing and in developing treatments for diseases arising from pathological adsorption-induced assembly. © 2009 The American Physical Society. [DOI: [10.1063/1.3077866](https://doi.org/10.1063/1.3077866)]

I. INTRODUCTION

Self-assembly processes in biology and manufacturing applications often occur in the presence of boundaries that can adsorb the assembling species. Adsorption affects the equilibrium solution concentration, and the adsorbed species may also self-assemble under favorable thermodynamic conditions. In general, the enthalpic and entropic parameters governing self-assembly on the boundary differ from those in solution, and an enhanced concentration of the assembling species at the boundary itself can promote self-assembly. This common physical situation naturally motivates the study of the competition between self-assembly in solution and on the boundary that arises from the coupling of self-assembly and adsorption. In the present paper, we focus on the thermodynamical regulation of self-assembly on the boundary, a process which is expected to differ significantly from the previously studied case of self-assembly in bulk solution.¹⁻³ Similar to phase separation, self-assembly can proceed either upon cooling or heating, while adsorption occurs exclusively upon cooling. Both cases should display different manifestations of the coupling between assembly and adsorption.

We were initially motivated to consider this problem by interesting measurements⁴ concerning the formation of collagen fibers on model substrates having surface energy gradients created by exposing a self-assembled monolayer to UV radiation. These experiments indicate that collagen fiber

assembles on the surface when the surface energy exceeds a “critical” value. Later, a similar trend has been found for the assembly of fibronectin fibers in the presence of a substrate (sulfonated polystyrene) having a charge density gradient.⁵ Other observations reveal an apparently enhanced assembly of Co nanoparticles upon segregation to a liquid-liquid interface.⁶ Although these self-assembly processes have not been subjected to quantitative analysis and nonequilibrium effects are clearly at issue, these observations suggest a robust tendency for the surface enrichment at an interface to promote enhanced self-assembly at the boundary. Clearly, if this phenomenon is general, then it provides a powerful way to regulate self-assembly processes in biology and manufacturing. For example, it would be easy to understand how clathrin assembly on a membrane could be switched on by simply changing the affinity of clathrin for the substrate upon which it adsorbs (e.g., through the adsorption onto the membrane of polar molecules that reduce the effective charge on the membrane,^{7,8} thus increasing the attractive interaction between the clathrin molecules and the membrane.)

Numerous studies document the phenomenon of surface self-assembly in the formation of the amyloid fibers associated with neurodegenerative diseases and with diseases arising from the pathological deposition of amyloid plaques on the walls of blood vessels and various tissues.⁹ Amyloid fibril structures (“protofibrils”) formed in the early stage of self-assembly can significantly influence the ion conductivity of cell membrane,¹⁰ an effect implicated in their toxicity. These fibrils also nucleate fibers into larger scale insoluble amyloid plaques¹¹ in the brain (and other organs), a process that can also contribute to disease.

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Studies of the surface-induced assembly of fibers¹² provide insights into the mechanism for the physical regulation of adsorption-induced assembly. For example, gangliocide molecules (a component of membrane rafts) directly induce the formation of the toxic amyloid protofibrils on membranes,¹³ a phenomenon that is greatly inhibited by increasing the concentration of other raft membrane molecules (e.g., cholesterol^{14,15}) or by simply reducing the gangliocide concentration. (Gangliocide molecules are also believed to be involved in a wide range of basic cellular processes, such as cell recognition and adhesion, signal transduction, or other cell regulation processes.¹⁶) Alternatively, the cholesterol concentration in membranes may be modulated by adding β -cyclodextrin to the solution, thus depleting cholesterol from the membrane.¹⁷ Other dipolar molecules, such as phloretin and exifone, associate with the membrane and inhibit amyloid fibril assembly by reducing the attractive interaction between the amyloid proteins and the membrane.⁸ Bile salts are effective at promoting the adhesion of polar molecules to membranes.⁷ Oxidative damage of cell membranes, which naturally accompanies aging (and exposure to certain nanoparticles^{18,19}), also alters the surface interaction between adsorbed amyloids and thereby produces surface-induced “accelerated amyloid aggregation”²⁰ into toxic protofibrils at the membrane surface. We suggest that the oxidative damage of cells and adsorption-induced amyloid fiber assembly may also play a role in the increased clinical incidence of Alzheimer disease following brain injury.²¹ Adsorption-induced assembly of amyloid fibers can even be demonstrated on common polar surfaces, such as mica and oxidized graphite.²² Pesticides can enhance amyloid fibrillation, and pesticide exposure is correlated with an increased incidence of Parkinson disease, one of a number of serious amyloid diseases.²³

Evidently, as a physical phenomenon, surface-induced amyloid formation is not particularly unusual. Many proteins (of both animal and plant origins) are capable of forming amyloid fibrils so that adsorption-induced self-assembly of protein fibers has wide significance for regulating self-assembly processes in biology, biofilm formation,^{24,25} biomineralization,²⁶ and in diseases associated with pathological self-assembly that is “nucleated” by substrates. Adsorption-induced self-assembly is also prevalent for synthetic molecules, such as cyclodextrin²⁷ and asphaltene molecules at the surface of oil-water dispersions,²⁸ and this phenomenon can also be expected for numerous synthetic gelator and nanoparticle systems. Surface-induced self-assembly obviously offers promise for the fabrication of new materials by directed assembly.^{29–32} For example, self-assembling proteins on surfaces are promising materials for extremely high density memory storage.³³

These numerous fragmentary observations of adsorption-induced self-assembly provide a motivation for investigating whether the competition between adsorption and self-assembly can produce a thermodynamic switching between self-assembly in solution and self-assembly on the substrate. Consequently, we address this question using a statistical mechanical model for the self-assembly and adsorption. Section II describes the theory used in our numerical studies of the competition between adsorption and self-

assembly in solution. Section III summarizes the computed thermodynamic properties for systems in which self-assembly in solution and on the surface proceed either upon cooling or heating. A special discussion is devoted to the switching of self-assembly on the surface by altering the interactions between monomers of the self-assembling species and the surface.

II. FLORY–HUGGINS-TYPE THEORY OF SELF-ASSEMBLY IN SOLUTION AND ON THE SURFACE

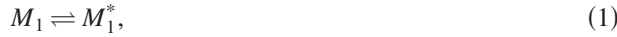
Self-assembly in biological systems often involves the concerted action of multiple thermodynamic transitions³⁴ that serve to activate the transition and to control the morphology of the assembly. For example, much discussion has been devoted to the development of liquid crystalline order in polymerizing systems^{35–37} and to consideration of the coupling between equilibrium polymerization, the helix-coil transition,^{38,39} and chain bundling,⁴⁰ and between self-assembly and phase separation.^{2,41,42} Self-assembly in living systems often occurs in the congested environment within the cell,⁴³ and the adsorption of the assembling species on boundaries must be common. This section describes a Flory–Huggins (FH)-type theory for these competing transitions, with focus on several basic thermodynamic properties, including the extent of polymerization, the average cluster size, and the fraction of the surface occupied by adsorbed species.

Although equilibrium polymerization theory was originally derived² for the self-assembly of linear polymer chains, the resulting mean field description is fairly *insensitive* to the topological structure of the assembling species. Consequently, the theory can be considered as a simplified or “minimal” model of self-assembly, just as FH theory provides a simplified general treatment of phase separation in polymer systems. Thus, the terms polymerization and self-assembly transition are used interchangeably below. However, the self-assembly of compact and branched polymer structures involves the formation of multifunctional contacts and the emergence of rigidity effects in the assembled species. Both these factors would have to be incorporated into the theory to ensure its applicability to these other types of self-assembly. Moreover, when the energy of the associative interaction becomes large compared to the thermal energy, then long times are required for particle clusters to reach equilibrium, and nonequilibrium “aggregates” ensue. As in our previous studies^{1–3,41} of self-assembly, attention is restricted to “self-assembly” processes in which cluster organization is governed by equilibrium thermodynamics.

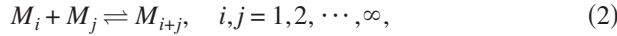
A. Lattice model of adsorption

Before adsorption and self-assembly, the surface contains N_l^* lattice sites that are all covered by N_l^* solvent molecules, while the N_l lattice sites in the bulk ($N_l \gg N_l^*$) are occupied by n_o^o solvent molecules and n_1^o monomers M_1 of the self-assembling species M . Under favorable circumstances, the monomers M_1 may adsorb on the surface. Since the system is taken, for simplicity, as being incompressible,

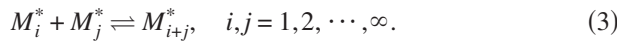
adsorption implies that the absorbing entities M_1 displace solvent molecules from the surface to the bulk, as schematically represented by the equilibrium,



where the number of the absorbed monomers M_1^* cannot exceed N_l^* . Apart from this constraint, reaction (1) is mathematically identical to the thermal activation step in equilibrium polymerization theory. The monomers M_1 may also self-associate in solution, and the self-association process is assumed to proceed in a fully democratic fashion,



that is simplest mode of association (termed the free association model).² The adsorbed species M_1^* may also self-assemble on the surface, and this process is likewise taken as free association,



The three processes in Eqs. (1)–(3) are assumed to proceed in equilibrium with the corresponding equilibrium constants (K_a, K_p, K_p^*),

$$K_a = \exp[-(\Delta h_a - T\Delta s_a)/(k_B T)], \quad (4)$$

$$K_p = \exp[-(\Delta h_p - T\Delta s_p)/(k_B T)], \quad (5)$$

and

$$K_p^* = \exp[-(\Delta h_p^* - T\Delta s_p^*)/(k_B T)], \quad (6)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and $(\Delta h_a, \Delta s_a)$, $(\Delta h_p, \Delta s_p)$, and $(\Delta h_p^*, \Delta s_p^*)$ are the enthalpies and entropies of monomer adsorption, polymerization in solution, and self-assembly on the surface, respectively. The total numbers of lattice sites in solution (N_l) and on the surface (N_l^*) are constants that may be expressed in terms of the compositions by

$$N_l = n_o^o + n_1^o = n_o^o + \sum_{i=1}^{\infty} in_i^* + \sum_{i=1}^{\infty} in_i = n_o + \sum_{i=1}^{\infty} in_i, \quad (7)$$

and

$$N_l^* = n_o^* + \sum_{i=1}^{\infty} in_i^*, \quad (8)$$

where n_i , n_o , n_i^* , and n_o^* designate the numbers of i -mers and solvent molecules in solution and on the surface, respectively. (The superscript * denotes a surface property.) Both solvent molecules and monomers of the self-associating species M occupy single lattice sites (in solution and on the surface), whereas a cluster M_i (or M_i^*) extends over i lattice sites. Excluded volume constraints preclude any two species from occupying a common lattice site.

Equations (7) and (8) are rewritten in more convenient forms that involve the volume fractions $\{\phi_\alpha\}$,

$$\phi_o^o + \phi_1^o = \phi_o + \sum_{i=1}^{\infty} \phi_i = 1, \quad (9)$$

with

$$\phi_o^o \equiv \frac{n_o + N_l^*}{N_l + N_l^*} \approx \frac{n_o}{N_l}, \quad \phi_1^o \equiv \frac{n_1^o}{N_l + N_l^*} \approx \frac{n_1^o}{N_l}, \quad \phi_o \equiv \frac{n_o}{N_l}, \quad (10)$$

$$\phi_i \equiv \frac{in_i}{N_l},$$

and

$$\phi_o^* + \sum_{i=1}^{\infty} \phi_i^* = 1, \quad (11)$$

with

$$\phi_o^* \equiv \frac{n_o^*}{N_l^*}, \quad \phi_i^* \equiv \frac{in_i^*}{N_l^*}. \quad (12)$$

The initial volume fractions ϕ_1^o and ϕ_o^o refer to the overall system, while equilibrium volume fractions are introduced separately for the solution $(\phi_o, \{\phi_i\})$ and for the surface $(\phi_o^*, \{\phi_i^*\})$.

B. Theoretical background

Standard FH theory is applied to the lattice model (described above) to examine the competition between adsorption and self-assembly. The use of classic FH theory naturally imposes the constraint of incompressibility. The conditions of chemical equilibrium imply equalities of the chemical potentials $\{\mu_\alpha\}$ of the reacting species,

$$\mu_1 = \mu_1^*, \quad (13)$$

$$\mu_i = i \mu_1, \quad i = 1, 2, \dots, \infty, \quad (14)$$

and

$$\mu_i^* = i \mu_1^*, \quad i = 1, 2, \dots, \infty, \quad (15)$$

where the superscript on μ_i^* refers to the chemical potential of i -mer on the surface.

Neglecting interactions between molecules in the bulk and those on the surface, the total Helmholtz free energy F_{tot} of the system is the sum,

$$F_{\text{tot}} = F_{\text{bulk}} + F_{\text{surf}} \quad (16)$$

of FH contributions from the solution (F_{bulk}) and from the surface (F_{surf}). The former is just

$$\begin{aligned} \frac{F_{\text{bulk}}}{N_l k_B T} = & \phi_o \ln \phi_o + \sum_{i=1}^{\infty} \frac{\phi_i}{i} \ln \phi_i + \sum_{i=2}^{\infty} \phi_i f_i \\ & + \chi_{MM} \left(\sum_{i=1}^{\infty} \phi_i \right)^2 + \chi_{oo} \phi_o^2 + 2\chi_{Mo} \phi_o \sum_{i=1}^{\infty} \phi_i, \end{aligned} \quad (17)$$

while the latter equals

$$\begin{aligned} \frac{F_{\text{surf}}}{N_l^* k_B T} &= \phi_o^* \ln \phi_o^* + \sum_{i=1}^{\infty} \frac{\phi_i^*}{i} \ln \phi_i^* + \sum_{i=1}^{\infty} \phi_i^* f_i^* \\ &+ \chi_{M^* M^*} \left(\sum_{i=1}^{\infty} \phi_i^* \right)^2 + \chi_{oo} (\phi_o^*)^2 + 2\chi_{M^* o} \phi_o^* \sum_{i=1}^{\infty} \phi_i^*, \end{aligned} \quad (18)$$

where the volume fractions $\{\phi_{\alpha}\}$ are defined by Eqs. (9)–(12) and f_i and f_i^* designate the specific Helmholtz free energies of single i -mers M_i and M_i^* , respectively. These quantities emerge from the FH theory for linear polymer chains as

$$f_i = \frac{1}{i} \ln \frac{2\gamma^2}{z^i} + \frac{i-1}{i} - \ln \gamma + \frac{i-1}{i} \frac{\Delta h_p - T\Delta s_p}{k_B T}, \quad i \geq 2, \quad (19)$$

and

$$f_1^* = \frac{\Delta h_a - T\Delta s_a}{k_B T}, \quad (20)$$

$$\begin{aligned} f_i^* &= \frac{1}{i} \ln \frac{2(\gamma^*)^2}{z^{*i}} + \frac{i-1}{i} - \ln \gamma^* + \frac{i-1}{i} \frac{\Delta h_p^* - T\Delta s_p^*}{k_B T} \\ &+ \frac{i}{i} \frac{\Delta h_a - T\Delta s_a}{k_B T}, \quad i \geq 2, \end{aligned} \quad (21)$$

where z and z^* are the lattice coordination numbers for the solution and the surface, respectively, and γ and γ^* are the stiffness parameters which equal unity for rigid chains (and dimers) and equal $z-1$ and z^*-1 for fully flexible chains ($i > 2$). (The specific free energy f_1 of a nonadsorbed monomer is taken to vanish.) The interaction parameters $\{\chi_{\alpha\beta} \propto 1/T\}$, ($\alpha, \beta \equiv M, M^*, o$) in Eqs. (17) and (18) represent the average van der Waals interactions between pairs of monomers of species α and β , ranging from monomers M_1 and M_1^* to solvent molecules labeled by the subscript o . For simplicity, unpolymerized monomers M_1 and M_1^* are taken as energetically equivalent to those in the clusters M_i and M_i^* , respectively.

The free energy expressions in Eqs. (17) and (18) enable evaluating the chemical potentials μ_i and μ_i^* , ($i \geq 1$) from the standard thermodynamic definitions,

$$\begin{aligned} \mu_i - i\mu_o &= \left. \frac{\partial F_{\text{bulk}}}{\partial n_i} \right|_{T, N_l, \{n_{j \neq i}\}} \\ &= i \left. \frac{\partial (F_{\text{bulk}}/N_l)}{\partial \phi_i} \right|_{T, N_l, \{\phi_{j \neq i}\}}, \quad i \geq 1, \end{aligned} \quad (22)$$

and

$$\begin{aligned} \mu_i^* - i\mu_o &= \left. \frac{\partial F_{\text{surf}}}{\partial n_i^*} \right|_{T, N_l^*, \{n_{j \neq i}^*\}} \\ &= i \left. \frac{\partial (F_{\text{surf}}/N_l^*)}{\partial \phi_i^*} \right|_{T, N_l^*, \{\phi_{j \neq i}^*\}}, \quad i \geq 1, \end{aligned} \quad (23)$$

where the appearance of the chemical potential μ_o of the solvent is due to the assumed system's incompressibility. Af-

ter some algebra, the equilibrium conditions in Eqs. (13)–(15) are transformed into relations between the volume fractions of the corresponding species in the reactions in Eqs. (2), (3), and (1),

$$\phi_i = iCA^i, \quad i \geq 2, \quad (24)$$

with

$$C \equiv \frac{z}{2\gamma^2 K_p}, \quad A \equiv \gamma\phi_1 K_p, \quad A < 1, \quad (25)$$

$$\phi_i^* = iC^*(A^*)^i, \quad i \geq 2, \quad (26)$$

with

$$C^* \equiv \frac{z^*}{2(\gamma^*)^2 K_p}, \quad A^* \equiv \gamma^*\phi_1^* K_p, \quad A^* < 1, \quad (27)$$

and

$$\phi_i^* = \phi_1 K_a \frac{1 - \sum_{i=1}^{\infty} \phi_i^*}{1 - \sum_{i=1}^{\infty} \phi_i} \exp \left[2\chi \sum_{i=1}^{\infty} \phi_i - 2\chi^* \sum_{i=1}^{\infty} \phi_i^* \right], \quad (28)$$

with

$$\chi \equiv \chi_{MM} + \chi_{oo} - 2\chi_{Mo}, \quad \chi^* \equiv \chi_{M^*M^*} + \chi_{oo} - 2\chi_{M^*o}. \quad (29)$$

Inserting Eqs. (24) and (26) into the sums of Eq. (28) and performing the summations lead to the more mathematically tractable form,

$$\begin{aligned} \phi_i^* &= \phi_1 K_a \frac{1 - \phi_1^* - \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}}{1 - \phi_1 - \frac{CA^2(2-A)}{(1-A)^2}} \exp \left\{ 2\chi \left[\phi_1 \right. \right. \\ &\left. \left. + \frac{CA^2(2-A)}{(1-A)^2} \right] - 2\chi^* \left[\phi_1^* + \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2} \right] \right\}. \end{aligned} \quad (30)$$

Equations (24) and (26) provide the recipe for evaluating the cluster size distributions in solution and on the surface, respectively. The distribution $\{\phi_i\}$ is determined once the concentration ϕ_1 of unpolymerized monomers in solution is evaluated. Similarly, knowledge of the concentration ϕ_1^* of adsorbed monomers on the surface enables computing $\{\phi_i^*\}$. These two unknowns are related to each other by Eq. (30) and the mass conservation condition,

$$n_1^o = n_1 + \sum_{i=2}^{\infty} i n_i + n_1^* + \sum_{i=2}^{\infty} i n_i^*. \quad (31)$$

Diving both sides of Eq. (31) by N_l , substituting Eqs. (24) and (26) for the resulting volume fractions, and performing the summations convert Eq. (31) into the form,

$$\begin{aligned} \frac{N_l + N_l^*}{N_l} \phi_1^o &= \phi_1 + \frac{CA^2(2-A)}{(1-A)^2} \\ &+ \frac{N_l^*}{N_l} \left[\phi_1^* + \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2} - \phi_1^o \right] \end{aligned} \quad (32)$$

that simplifies further (because $N_l^* \ll N_l$) into the relation

$$\phi_1^o \approx \phi_1 + \frac{CA^2(2-A)}{(1-A)^2}, \quad (33)$$

which also appears in equilibrium polymerization theory for the free association model.² Equation (33) allows determining ϕ_1 numerically. Likewise, the second unknown concentration ϕ_1^* is determined by solving Eq. (30) (numerically). The use of Eq. (33) transforms the latter into the expression

$$\phi_i^* \approx \phi_1 K_a \frac{1 - \phi_1^* - \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}}{1 - \phi_1^o} \exp \left\{ 2\chi\phi_1^o - 2\chi^* \left[\phi_1^* + \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2} \right] \right\}. \quad (34)$$

While $\{\phi_i\}$ are independent of the solute-solvent interactions, the surface concentrations depend on χ and χ^* . For simplicity, we set $\chi = \chi^* = 0$, thereby reducing Eq. (34) to

$$\phi_i^* \approx \phi_1 K_a \frac{1 - \phi_1^* - \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}}{1 - \phi_1^o}. \quad (35)$$

Once the concentrations ϕ_1 and ϕ_1^* are determined by solving Eqs. (33) and (34), basic thermodynamic quantities can be easily evaluated. For instance, the extent of self-assembly in solution (Φ) is defined as a fraction of monomers of species M in the liquid state that are converted into clusters $\{M_i\}$ and is readily computed as

$$\Phi \equiv \frac{\sum_{i=2}^{\infty} in_i}{\sum_{i=1}^{\infty} in_i} = \frac{\sum_{i=2}^{\infty} \phi_i}{\sum_{i=1}^{\infty} \phi_i} \approx \frac{\phi_1^o - \phi_1}{\phi_1^o}, \quad (36)$$

which is a simple function of ϕ_1 and the initial monomer concentration ϕ_1^o . Similarly, the extent of self-assembly Φ_s on the surface, defined as

$$\Phi_s \equiv \frac{\sum_{i=2}^{\infty} in_i^*}{\sum_{i=1}^{\infty} in_i^*} = \frac{\sum_{i=2}^{\infty} \phi_i^*}{\sum_{i=1}^{\infty} \phi_i^*} = \frac{\frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}}{\phi_1^* + \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}}, \quad (37)$$

may be expressed in terms of ϕ_1^* and C^* and A^* of Eq. (27). The fraction θ of the surface occupied by adsorbed species simply equals

$$\theta \equiv \sum_{i=1}^{\infty} \phi_i^* = \phi_1^* + \frac{C^*(A^*)^2(2-A^*)}{(1-A^*)^2}. \quad (38)$$

The extent of self-assembly on the surface (Φ_s) and in solution (Φ) and the surface fraction θ are basic order parameters for the self-assembly and adsorption thermodynamic transitions. The inflection points of $\Phi_s(T, \phi_1^o = \text{const})$, $\Phi(T, \phi_1^o = \text{const})$, and $\theta(T, \phi_1^o = \text{const})$ as a function of temperature T define the surface assembly, bulk assembly, and the adsorption temperatures, respectively. As shown below, two adsorption temperatures can be defined when adsorption occurs upon cooling and self-assembly proceeds upon heating. The average cluster size L in solution becomes

$$L \equiv \frac{\sum_{i=1}^{\infty} in_i}{\sum_{i=1}^{\infty} n_i} = \frac{\sum_{i=1}^{\infty} \phi_i}{\sum_{i=1}^{\infty} \phi_i/i} \approx \frac{\phi_1^o}{\phi_1^o + CA^2/(1-A)}, \quad (39)$$

while the average cluster size L_s on the surface is obtained as

$$L_s \equiv \frac{\sum_{i=1}^{\infty} in_i^*}{\sum_{i=1}^{\infty} n_i^*} = \frac{\sum_{i=1}^{\infty} \phi_i^*}{\sum_{i=1}^{\infty} \phi_i^*/i} = 1 + \frac{\frac{C^*(A^*)^2}{(1-A^*)^2}}{\phi_1^* + \frac{C^*(A^*)^2}{1-A^*}}, \quad (40)$$

and L and L_s likewise emerge as simple functions of ϕ_1 and ϕ_1^* , respectively. Qualitatively, an increase in L and L_s should correspond to an increase in the viscosities of the bulk solution and the surface. The exact nature of this increase depends on the particular hydrodynamic model for these viscosity changes.

III. RESULTS

The model in Sec. II for the competition between surface adsorption and self-assembly in solution contains six free energy parameters, i.e., the enthalpies and entropies of adsorption ($\Delta h_a, \Delta s_a$), self-assembly in solution ($\Delta h_p, \Delta s_p$), and self-assembly on the surface ($\Delta h_p^*, \Delta s_p^*$). While adsorption generally occurs only upon cooling ($\Delta h_a < 0, \Delta s_a < 0$), both self-assembly processes can proceed either upon cooling ($\Delta h_p < 0, \Delta s_p < 0, \Delta h_p^* < 0, \Delta s_p^* < 0$) or upon heating ($\Delta h_p > 0, \Delta s_p > 0, \Delta h_p^* > 0, \Delta s_p^* > 0$). Our illustrative calculations below describe both cases of competitive adsorption and self-assembly, focusing on systems in which self-assembly on the surface dominates over that in solution. The stiffness parameters γ and γ^* in Eqs. (25) and (27) are set to unity (i.e., all clusters are treated as stiff structures), and the lattice coordination number in solution (z) and on the surface (z^*) are taken as $z=6$ and $z^*=4$ (corresponding to simple cubic and simple square lattices, respectively).

A. Self-assembly and adsorption upon cooling

When adsorption and self-assembly proceed upon cooling, all free energy parameters are generally negative. For simplicity, the enthalpies Δh_p and Δh_p^* and the entropies Δs_p and Δs_p^* of self-assembly in solution and on the surface are set equal, -35 kJ/mol and -105 J/mol K, respectively, values characteristic of the polymerization of poly(α -methyl styrene) in methylcyclohexane⁴⁴ and used in our previous examination of equilibrium polymerization.^{1,3,41} The enthalpy Δh_a of adsorption is varied and thus allowed to differ from the association enthalpy $\Delta h_p = \Delta h_p^*$. The entropies $\Delta s_a, \Delta s_p,$ and Δs_p^* are also chosen to be equal [$\Delta s_a = \Delta s_p^* = \Delta s_p = -105$ J/mol K].

Figure 1 presents the extent of self-assembly in solution (Φ) and on the surface (Φ_s) as a function of temperature T for fixed initial monomer concentration $\phi_1^o = 0.1$. The solid curves indicate the order parameter $\Phi_s(T)$ for self-assembly on the surface and from left to right correspond to $\Delta h_a = -35, -50,$ and -70 kJ/mol, while the dashed curve denotes $\Phi(T)$, which is independent of Δh_a (and Δh_p^*). Both $\Phi(T, \phi_1^o = \text{const})$ and $\Phi_s(T, \phi_1^o = \text{const})$ saturate to unity at low temperatures and approach zero at high temperatures, a behavior typical for the order parameter of systems self-assembling upon cooling.² Inspection of Fig. 1 also reveals that increasing $|\Delta h_a|$ leads to a predominance of surface assembly over assembly in solution (i.e., to $\Phi_s \gg \Phi$). For instance, when $\Delta h_a = -70$ kJ/mol, Φ_s exceeds Φ over the whole temperature range considered ($200 \text{ K} \geq T \geq 600 \text{ K}$).

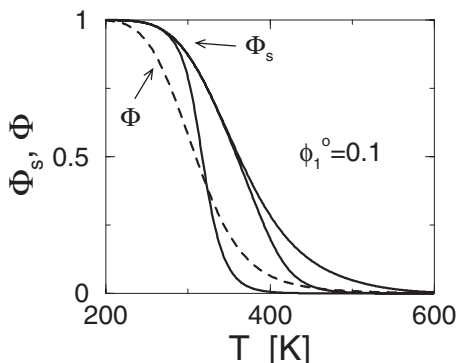


FIG. 1. The extent of self-assembly in solution (Φ) and on the surface (Φ_s) as a function of temperature T for fixed initial monomer concentration $\phi_1^o = 0.1$ when all three self-assembly processes (adsorption on the surface and self-assembly in solution and on the surface) occur upon cooling [$\Delta h_p^* = \Delta h_p = -35$ kJ/mol, $\Delta h_a < 0$, and $\Delta s_a = \Delta s_p^* = \Delta s_p = -105$ J/mol K]. The solid curves represent the order parameter $\Phi_s(T)$ for surface self-assembly and from left to right correspond to $\Delta h_a = -35$, -50 , and -70 kJ/mol, while the dashed curve denotes $\Phi(T)$, which is independent of Δh_a and Δh_p^* .

This trend is even more noticeable in Fig. 2(a) which exhibits $\Phi_s(T, \phi_1^o = \text{const})$ and $\Phi(T, \phi_1^o = \text{const})$, along with the fractions of the surface occupied by the adsorbed species [$\theta(T, \phi_1^o = 0.1)$] and by monomers [$\phi_1^*(T, \phi_1^o = 0.1)$] for the model illustrated in Fig. 1 ($\Delta h_a = -70$ kJ/mol). When $|\Delta h_a| > |\Delta h_p^*| = |\Delta h_p|$, surface coverage invariably becomes more complete. The enhanced self-assembly on the surface over that in solution extends over a wide concentration range, as emphasized by Fig. 2(b) which presents Φ_s and Φ as a function of the initial monomer concentration at fixed temperature $T = 350$ K. The insensitivity of Φ_s and ϕ_1^* to ϕ_1^o in Fig. 2(b) is a consequence of the complete coverage of the surface by adsorbed species at $T = 350$ K (due to the relatively large adsorption enthalpy $|\Delta h_a| = 70$ kJ/mol). Increasing ϕ_1^o only causes an increase in $\{\phi_i\}$ and Φ in solution. More favorable free energy parameters for monomer adsorption than for self-assembly lead to a greater average cluster size on the surface (L_s) than in solution (L). Figure 3 quantifies this trend by illustrating the temperature variation of both L and L_s for the same model system as in Figs. 2(a) and 2(b) ($\Delta h_a = -70$ kJ/mol). The dominance of Φ_s over Φ [that is already found for systems with $|\Delta h_a| \Delta h_p^* = |\Delta h_p|$; see Figs. 1 and 2(a)] increases when the absolute enthalpy $|\Delta h_p^*|$ of self-assembly on the surface exceeds $|\Delta h_p|$.

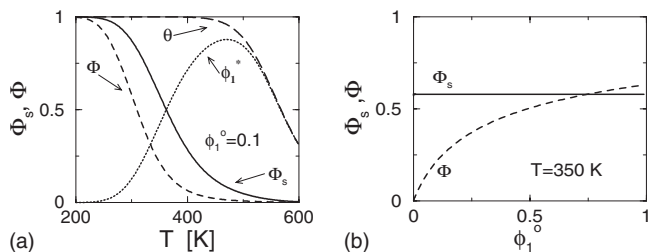


FIG. 2. The extent of self-assembly in solution (Φ) and on the surface (Φ_s) as a function of temperature T (a) and of the initial monomer concentration ϕ_1^o (b) for the system illustrated in Fig. 1 ($\Delta h_a = -70$ kJ/mol). The fraction θ of the surface occupied by adsorbed species equals unity at $T = 350$ K over the whole concentration range and the concentration of adsorbed monomers ϕ_1^* is constant and less than Φ_s for all ϕ_1^o and $T = 350$ K.

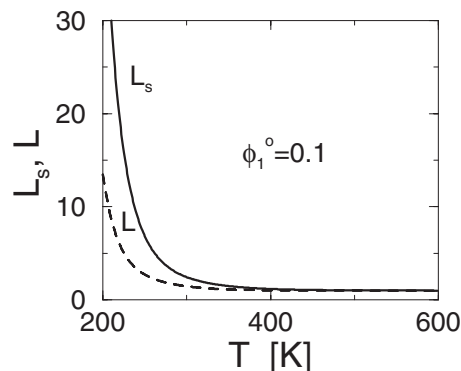


FIG. 3. The temperature variation of the average cluster size in solution (L) and on the surface (L_s) for one of the model system in Fig. 1 ($\Delta h_a = -70$ kJ/mol).

B. Self-assembly upon heating and adsorption upon cooling

A more complicated competition between adsorption and self-assembly in solution arises when self-assembly occurs upon heating and adsorption proceeds upon cooling. The simplest model for this self-assembly system is analyzed in Figs. 4–6, where we take $\Delta h_p = \Delta h_p^* = -\Delta h_a$. Figures 4(a) and 4(b) illustrate the order parameters $\Phi(T)$ and $\Phi_s(T)$ as a function of temperature T for a few fixed initial concentrations ϕ_1^o , respectively. The order parameter $\Phi(T, \phi_1^o = \text{const})$ for self-assembly in solution saturates to unity at high temperatures T , in contrast to $\Phi(T, \phi_1^o = \text{const})$ in Figs. 1 and 2(a) where Φ approaches unity at low temperatures. A more non-trivial behavior emerges, however, for the order parameter $\Phi_s(T, \phi_1^o = \text{const})$ of self-assembly on the surface. Specifically, $\Phi_s(T, \phi_1^o = \text{const})$ varies *nonmonotonically* with temperature and exhibits a maximum that stems from a competition between adsorption (proceeding upon cooling) and self-assembly (occurring upon heating). A nonmonotonic variation of the order parameter Φ has been observed for the polymerization of G-actin (where a competition between activated dimerization and propagation is responsible for this effect),^{45,46} so that this odd behavior is not without precedence.

The fraction $\theta(T, \phi_1^o = \text{const})$ of the surface occupied by adsorbed species increases monotonically upon cooling [see Fig. 5(a)], similar to the extent of self-assembly Φ in Fig. 1.

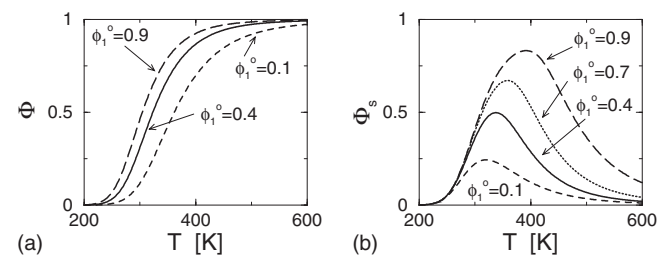


FIG. 4. The temperature variation of the extent of self-assembly in solution [Φ ; (a)] and on the surface [Φ_s ; (b)] when monomer adsorption proceeds upon cooling [$\Delta h_a = -35$ kJ/mol, $\Delta s_a = -105$ J/mol K], while self-assembly in solution and on the surface occur upon heating ($\Delta h_p^* = \Delta h_p = -\Delta h_a = 35$ kJ/mol, $\Delta s_p^* = \Delta s_p = -\Delta s_a = 105$ J/mol K). Different curves correspond to the indicated initial monomer concentrations ϕ_1^o . This simple model of self-assembly is further analyzed in Figs. 5 and 6.

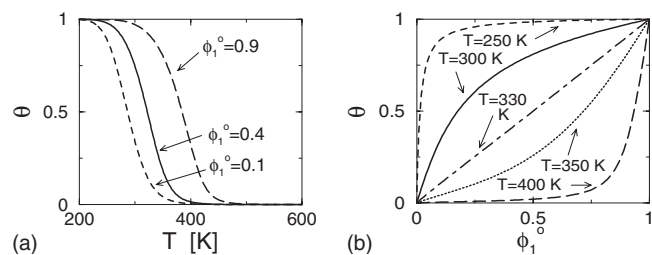


FIG. 5. The fraction θ of the surface occupied by adsorbed species as a function of temperature T (a) and of initial monomer concentration ϕ_1^o (b) for the model system considered in Fig. 4.

At sufficiently low temperatures, $\theta(T, \phi_1 = \text{const})$ is close to unity since the surface becomes almost entirely covered by monomers as the temperature decreases ($\Delta h_a < 0, \Delta s_a < 0$). The adsorbed monomers cannot, however, assemble into larger clusters at low temperatures due to the unfavorable free energy parameters Δh_p^* and Δs_p^* ($\Delta h_p^* > 0, \Delta s_p^* > 0$). Temperature likewise qualitatively influences the composition dependence of $\theta(\phi_1^o, T = \text{const})$. As displayed in Fig. 5(b), the function $\theta(\phi_1^o, T = \text{const})$ is concave at high temperatures, strictly linear (with the slope equal to unity) at intermediate temperatures, e.g., $T = 330$ K, and is convex at low temperatures. By definition, θ does not convey information about the cluster size distribution on the surface, but this information is reflected in the average cluster sizes in solution (L) and on the surface (L_s). These properties evidently also manifest, in a fashion similar to Φ and Φ_s , the competition between adsorption-induced assembly on the boundary and self-assembly in solution. Figures 6(a) and 6(b) present the temperature variation of L and L_s , respectively, for a few fixed initial monomer concentrations ϕ_1^o . The average cluster size $L(T, \phi_1^o = \text{const})$ in solution grows monotonically with temperature, and the average cluster size $L_s(T, \phi_1^o = \text{const})$ on the surface exhibits similar maxima to those for $\Phi_s(T, \phi_1^o = \text{const})$ in Fig. 4(b). Moreover, the maxima of $\Phi_s(T)$ and $L_s(T)$ occur at the same temperatures.

More realistically, the enthalpies of adsorption ($|\Delta h_a|$) and self-association $\Delta h_p^* = \Delta h_p$ are different. Increasing the absolute enthalpy $|\Delta h_a|$ of adsorption relative to $|\Delta h_p^*| = |\Delta h_p|$ simply enhances the difference between the order parameters Φ_s and Φ , pushing Φ_s toward higher values of unity. The average cluster size L_s on the surface again exhibits a maximum as a function of temperature whose magnitudes grow with $|\Delta h_a|$. Moreover, the disparity between L_s and the average cluster size L in solution (which increases

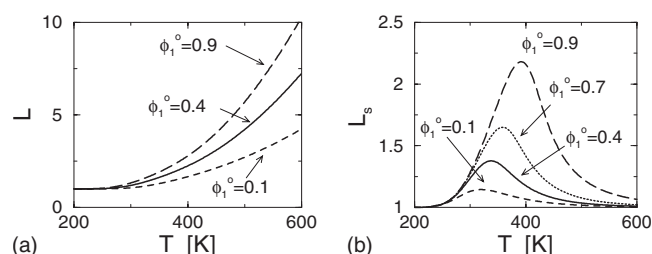


FIG. 6. The temperature variation of the average cluster size in solution [L ; (a)] and on the surface [L_s ; (b)] for the model system analyzed in Fig. 4. Different curves correspond to the indicated initial monomer concentrations ϕ_1^o .

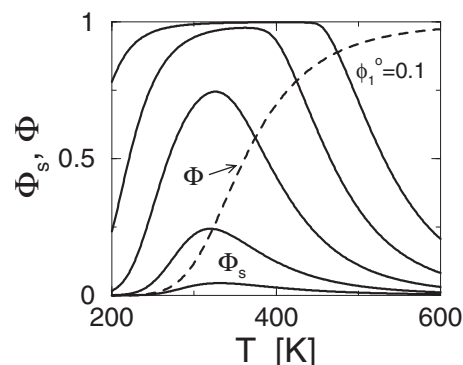


FIG. 7. The extent of self-assembly in solution (Φ) and on the surface (Φ_s) as a function of temperature T for a series of model systems where monomer adsorption occurs upon cooling and self-assembly proceeds upon heating. The systems differ from those analyzed in Figs. 4–6 by allowing Δh_p^* to depart from Δh_p [$\Delta h_p = -\Delta h_a = 35$ kJ/mol, $\Delta s_p = \Delta s_p^* = -\Delta s_a = 105$ J/mol K and $\Delta h_p^* \neq \Delta h_p$]. The solid curves represent $\Phi_s(T, \phi_1^o = \text{const})$ and from bottom to top correspond to $\Delta h_p^* = 40, 35, 30, 25$, and 20 kJ/mol. The dashed curve denotes $\Phi(T, \phi_1^o = \text{const})$, which is independent of the magnitude of Δh_p^* .

monotonically with temperature) remains over a wide temperature range ($200 \text{ K} \leq T \leq 400 \text{ K}$). A larger $|\Delta h_a|$ also implies an increased fraction θ of surface covered by the adsorbed species.

The most physically interesting case involving a strong competition between adsorption on cooling and self-assembly on heating arises when the enthalpies for self-assembly in solution and on the surface differ ($\Delta h_p^* \neq \Delta h_p = -\Delta h_a = 35$ kJ/mol). Figure 7 displays the extent of polymerization in solution (Φ) and on the surface (Φ_s) as a function of temperature T . The solid curves represent $\Phi_s(T, \phi_1^o = 0.1)$ and from bottom to top correspond to $\Delta h_p^* = 40, 35, 30, 25$, and 20 kJ/mol. The dashed curve denotes $\Phi(T, \phi_1^o = 0.1)$, which is independent of Δh_p^* . A smaller Δh_p^* (when $\Delta h_p^* > 0$) implies that self-assembly begins at lower temperatures and Φ_s grows. When Δh_p^* is sufficiently small (for instance, 20 kJ/mol in Fig. 7), $\Phi_s(T, \phi_1^o = \text{const})$ is close to unity over a wide temperature range ($300 \text{ K} \leq T \leq 450 \text{ K}$). Thus, the segregation of the self-assembling species M between the surface and solution is almost complete at low temperatures. The average cluster size $L_s(T, \phi_1^o = \text{const})$ on the surface is also a parabolic function of temperature (see Fig. 8), and L_s considerably exceeds L at low and intermediate temperatures. At a fixed temperature, $L_s(T = \text{const}, \phi_1^o)$ rapidly approaches a constant with increasing initial monomer concentration ϕ_1^o . Figures 7 and 8 illustrate a situation where essentially no self-assembly occurs in solution, while self-assembly is appreciable on the substrate.

C. Switching surface self-assembly through a change in surface interaction

Many proteins, such as actin, tubulin, or the capsid structures of some viruses (e.g., tobacco mosaic virus) exhibit (“entropy driven”) self-assembly upon heating, as mentioned before.^{45,47,48} This mode of assembly has been established in the formation of neurofibrillary tangles, which are paired helical filaments of the protein tau that appear in conjunction with amyloid protein fibers in Alzheimer’s disease.⁴⁹ As-

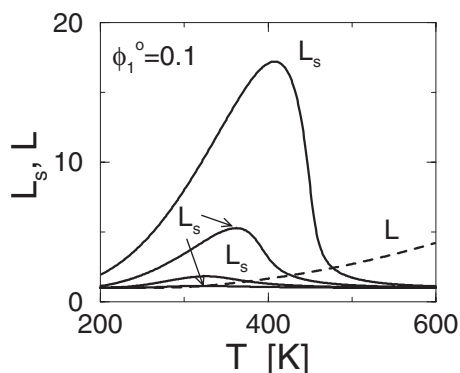


FIG. 8. The average cluster size in solution (L) and on the surface (L_s) as a function of temperature T for the series of model systems considered in Fig. 7. The solid curves denote $L_s(T, \phi_1^o = \text{const})$ and from bottom to top correspond to $\Delta h_p^* = 35, 30, 25,$ and 20 kJ/mol. The dashed curve indicates $L(T, \phi_1^o = \text{const})$ that is insensitive to the magnitude of Δh_p^* .

sembly on heating is prevalent in aqueous solutions because protein clustering releases some of the water molecules associated with isolated solvated proteins, thus *increasing* the entropy of the whole system. This type of assembly is thought to occur in clathrin assembly as well,⁴⁷ but thermodynamic measurements are limited for this material. The particular relevance of this category of self-assembly to biophysical systems provides impetus for considering how adsorption-induced assembly operates in these systems.

Focus now on the situation indicated in Fig. 7 where the enthalpies of association on the surface and in solution differ, $\Delta h_p^* = 20$ kJ/mol and $\Delta h_p = 35$ kJ/mol, and where the enthalpy Δh_a of adsorption is reasonably strong, i.e., $\Delta h_a = -\Delta h_p = -35$ kJ/mol. For simplicity, consider a system at room temperature $T = 298$ K and with the initial monomer concentration $\phi_1^o = 0.1$ for illustration. The order parameter Φ_s for self-assembly on the surface and the average chain length L_s are $\Phi_s(T = 298 \text{ K}, \phi_1^o = 0.1) = 0.99$ and $L_s(T = 298 \text{ K}, \phi_1^o = 0.1) = 7.84$, while Φ and L in solution are $\Phi(T = 298 \text{ K}, \phi_1^o = 0.1) = 0.11$ and $L(T = 298 \text{ K}, \phi_1^o = 0.1) = 1.06$. Self-assembly on the surface is thus appreciable, but assembly in solution is rather limited. Now, assume that the enthalpy of adsorption is reduced by a factor of 3, a reduction that can be achieved, for instance, by adding to the system a small amount of some chemical species that exhibits a very high affinity for the adsorbing substrate. The above alteration in the surface interaction sharply diminishes Φ_s and L_s to $\Phi_s(T = 298 \text{ K}, \phi_1^o) = 0.014$ and $L_s(T = 298 \text{ K}, \phi_1^o) = 1.01$, while Φ and L in the bulk remain invariant. Removing the added chemical species from the system restores Δh_a to its initial value and leads to a regeneration of assembly on the surface. The self-assembly process can thus be *switched* in response to the adsorption of another species on the substrate. As a concrete example of this phenomenon, we note that clathrin molecules fully self-assemble into stable hexagonal sheet polymers on the plasma membrane surface of fixed cells (depleted of cholesterol through the introduction of cyclodextrin to enhance clathrin binding), and that the introduction of auxilin molecules seems to trigger the separation of the clathrin lattice from the membrane.⁵⁰

The control of this switching process requires reasonable

control of temperature. When temperature is increased, self-assembly in solution then seriously competes with association on the surface, while if temperature is lowered, self-assembly in solution and on the surface both become unfavorable, regardless of the strength of the surface adsorption interaction. Thus, an intermediate temperature window exists in which the competition between adsorption and self-assembly on the boundary and in solution creates conditions highly favoring assembly on the substrate and not in solution.

Reducing the temperature too much renders the switching inoperative, thereby providing a clear means of identifying adsorption-induced assembly. For example, the assembly of clathrin into hexagonal lattice cage structures on cell membranes is an important cellular process related to the translocation of small particles (such as viruses and nanoparticles) through the cell membrane. Under *in vivo* conditions, this cage formation process has been found to *cease* with sufficient cooling.⁵¹ This observation accords with our hypothesis that adsorption-induced self-assembly regulates this crucial biological self-assembly process.

Switching between surface-induced assembly and disassembly is also possible when both assembly and adsorption occur upon cooling. Consider a system where the magnitudes of the enthalpies of surface adsorption and surface assembly are large compared to the absolute enthalpy of self-assembly in solution (e.g., $\Delta h_a = -70$ kJ/mol, $\Delta h_p^* = -50$ kJ/mol, and $\Delta h_p = -35$ kJ/mol). The addition to the system of an extra surface active species (that reduces Δh_a , say by a factor of 3) implies that the order parameter Φ_s , e.g., at the temperature $T = 400$ K and initial concentration $\phi_1^o = 0.1$, drops from 0.94 to 0.017, while the order parameter for self-assembly in solution remains small and invariant ($\Phi = 0.065$). No assembly appears in the system in the high temperature limit. The introduction of additional constraints on the self-assembly and adsorption processes, such as thermal activation, chemical initiation, topological constraints, etc., normally influences the rate of variation of the order parameters with temperature and consequently of the transition “cooperativity.”³ Higher cooperativity should enhance the sensitivity of the switching of the assembly to the interaction energy with the surface.

IV. DISCUSSION

As described above, many biological processes appear to be initiated through the selective adsorption onto substrates of proteins and/or other biological macromolecules, followed by their self-assembly into functional structures or toxic layers. The emulation of this adsorption-induced assembly process for nanomanufacturing and sensing applications is obviously attractive, but our theory clearly establishes that this type of assembly process must be tightly regulated thermodynamically. However, most observations of surface-induced self-assembly have only been qualitative, and, we, stress the need for a fundamental theory describing how monomer adsorption regulates self-assembly and allowing better quantification of the thermodynamic interaction parameters governing this type of directed assembly.

We develop and apply a statistical mechanical theory to

describe the coupling of adsorption and self-assembly based on a FH-type (equilibrium polymerization) model of self-assembly and the standard Langmuir model of adsorption. The resulting theory should suffice to capture essential thermodynamic characteristics of this phenomenon since this kind of simple mean field treatment has been successfully utilized in modeling the assembly of structural biological proteins into fibers.⁵²⁻⁵⁵

The competition between adsorption (combined with successive self-assembly on the surface) and self-assembly in solution is examined here as a function of the enthalpies and entropies of three equilibrium processes, adsorption of monomers on the surface, their self-assembly on a substrate, and self-assembly in solution. For simplicity, the short range van der Waals interactions of the self-assembling entities and solvent molecules are neglected in the illustrative analysis in Sec. III, although the formalism developed in Sec. II includes these interactions. Our illustrative calculations focus primarily on systems in which equilibrium polymerization on the surface predominates over equilibrium polymerization in solution. To reduce the number of variable parameters, we assume identical (absolute) entropies of adsorption (Δs_a), self-assembly on the surface (Δs_p^*), and in solution (Δs_p), so that the enthalpies of adsorption (Δh_a), assembly on the surface (Δh_p^*), and assembly in solution (Δh_p) are the only energetic model parameters treated as variables. While adsorption generally occurs upon cooling ($\Delta h_a < 0, \Delta s_a < 0$), self-assembly can proceed either upon cooling ($\Delta h_p^* < 0, \Delta s_p^* < 0, \Delta h_p < 0, \Delta s_p < 0$) or heating ($\Delta h_p^* > 0, \Delta s_p^* > 0, \Delta h_p > 0, \Delta s_p > 0$). For the simplest reference case where $\Delta h_a, \Delta h_p^*$, and Δh_p are negative and equal, the extent of polymerization Φ_s on the surface is found to exceed slightly its counterpart Φ in solution over a narrow range of temperatures and concentrations. Making Δh_a somewhat more negative (e.g., $\Delta h_a = 2\Delta h_p = 2\Delta h_p^*$), so that monomer adsorption is favored over self-assembly on the surface and in solution) enhances the differences $\Phi_s(T, \phi_1^o = \text{const}) - \Phi(T, \phi_1^o = \text{const})$ and $\Phi_s(\phi_1^o, T = \text{const}) - \Phi(\phi_1^o, T = \text{const})$, but the magnitudes of Φ_s and Φ remain rather similar. A larger enhancement of Φ_s over Φ emerges, however, when both $|\Delta h_a|$ and $|\Delta h_p^*|$ are greater than the enthalpy of association in solution (e.g., $|\Delta h_p| > |\Delta h_p^*| > |\Delta h_p|$). Systems with adsorption and self-assembly on cooling are generally characterized by a monotonic decrease of all order parameters (Φ, Φ_s, θ) with temperature, and trends for other properties, such as the average cluster mass (chain length), are similar to those for equilibrium self-assembly in solution,² except for the possibility of having more or less assembly on the boundary relative to that in solution. Changing the energetic parameters can significantly alter the relative ordering of the adsorption and self-assembly processes upon cooling, and this alteration can in some instances produce considerable enhancement of self-assembly on the surface over that in solution.

The occurrence of both assembly processes (on the surface and in solution) on heating leads to significant variability in the phenomena induced by the competition between adsorption and self-assembly. One consequence of this competition is reflected in the appearance of a nonmonotonic temperature dependence and a maximum for the order pa-

rameter $\Phi_s(T, \phi_1^o = \text{const})$ and the average cluster size $L_s(T, \phi_1^o = \text{const})$ for surface self-assembly. In contrast, the corresponding quantities in solution (Φ and L) grow monotonically with temperature. The maximum in $\Phi_s(T, \phi_1^o = \text{const})$ and $L_s(T, \phi_1^o = \text{const})$ and the difference $\Phi_s(T, \phi_1^o = \text{const}) - \Phi(T, \phi_1^o = \text{const})$ grow with an increase in the adsorption enthalpy ($|\Delta h_a| > |\Delta h_p^*| = |\Delta h_p|$) and with a decrease in the enthalpy Δh_p^* (see Figs. 7 and 8 referring to $\Delta h_p^* \leq \Delta h_p = |\Delta h_a|$). Qualitatively, the nonmonotonic variation of Φ_s in Figs. 4(b) and 7 resembles the temperature dependence of the order parameter Φ for actin polymerization in solution,^{45,46} and ramifications of the competition between activation and propagation of assembly appear in a wide class of other equilibrium polymerization models.² Similarly, the reentrant temperature variation of Φ_s resembles a closed loop phase boundary, where upon starting from a self-assembled state point within the closed loop, sufficient heating or cooling restores the system to a homogeneous unclustered particle state.

We also analyze how the switching of self-assembly on boundaries might operate for systems self-assembling either on cooling or heating. Reducing the magnitude of the surface adsorption can cause a dramatic disassembly of the surface assembled chains when self-assembly occurs on heating. The same qualitative behavior can arise for self-assembly on cooling if the enthalpy for the surface adsorption is decreased by, for instance, addition of a surface active species, thereby reinforcing the certainty of the possibility of observing instances of a transition between surface assembly and disassembly by varying the surface boundary condition.

ACKNOWLEDGMENTS

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