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Coupling between a first-order gas-liquid phase transition and a second-order orientational transition in Langmuir monolayers

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The Ginzburg-Landau theory is developed to investigate coupling between a gas-liquid first-order phase transition (FOPT) and an orientational second-order phase transition (SOPT) in Langmuir monolayers. It is found that the coupled SOPT and FOPT takes place simultaneously if the uncoupled FOPT occurs prior to the SOPT with compression, and that in the opposite case, the coupling makes the FOPT take place at a lower pressure, but still behind the SOPT. Gas-liquid phase separation always leads to a decrease in the averaged order parameter of the orientational phase transition, which is qualitatively consistent with experimental data. [S1063-651X(99)08411-1]

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I. INTRODUCTION

Coupled phase transitions have drawn a considerable amount of attention, in particular the coupling between a first-order phase transition (FOPT) and a second-order phase transition (SOPT). Such a coupling exists widely in many phase transitions accompanied with phase separation tendencies. For example, in oxygen-doped La_2CuO_{4+z}, a low concentration of holes as well as excess interstitial oxygen atoms may drive a macroscopic phase separation into a metallic superconducting hole-rich ($z \simeq 0.055$) and an insulating antiferromagnetic hole-poor ($z \simeq 0.012$) phases [1]. The FOPT with the phase separation is evidently coupled with the SOPT, such as the superconducting phase transition in the hole-rich region or the magnetic phase transition in the hole-poor region. Manganese oxides are another example. Both experimental measurements and theoretical calculations have revealed a rich phase diagram in which there exist various magnetic, orbital, and charge orders. The phase separation tendency not only leads to a charge inhomogeneity, but also affects greatly competitions between ferromagnetism, antiferromagnetism, and paramagnetism [2]. As a result, it is highly desirable to understand fully coupled effects between a FOPT and a SOPT.

A Langmuir monolayer [3], which is composed of insoluble rodlike polymer molecules at an air-water interface, provides an ideal and simple model system for studying the coupled effects between a FOPT and a SOPT. In a monolayer of polar molecules there are two kinds of phase transitions. One is two-dimentional gas-liquid or liquid-solid transition, which is determined by the spatial distribution of hydrophilic heads of the molecules on the air-water interface. The other is the orientational phase transition of the rodlike molecules. An applied lateral pressure compressing molecular area can lead to a FOPT from a gaseous state to a liquid state. This compression can also result in a SOPT of molecular orientation from an isotropic phase into a polar phase with preferential alignment [4,5].

These phase transitions in the Langmuir monolayer have been studied for a long time by measurements of surface pressure-area isotherms [6]. By using a Maxwell displacement current-measured technique [7], Iwamoto *et al.* [8] recently observed the positional and orientational phase transitions in Langmuir films of liquid-crystal 4-cyano-4’-5-alkylbiphenyl (5CB), 7CB, 8CB, and 10CB. Theoretical calculations [4] of considering the orientational phase transition alone predicted that, as soon as the SOPT occurs, its polar order parameter increases rapidly with decreasing the molecular area. The increasing rate predicted is found much greater than that observed by experiments [8]. This disparity may stem from the fact that the coupled effects of the gas-liquid phase transition on the orientational phase transition was not taken into account there.

Recently, we developed a Ginzburg-Landau theory to study the coupling between a FOPT and a SOPT and obtained a qualitative agreement between theory and experiment [5]. In that theory, however, there was an artificial assumption that the uncoupled FOPT and SOPT take place at the same pressure. Besides, in that calculation, the prefactor of the free-energy density for the FOPT was assumed to be much greater than that of the SOPT term as well as the coupling term, i.e., only unilateral influence of the FOPT on the SOPT was considered. In this paper, we consider two different cases in which the uncoupled FOPT occurs prior to and behind the uncoupled SOPT, respectively. They are undoubtedly the most general and reasonable starting points. Besides, the prefactors of the free-energy densities for the

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FOPT, SOTP, and their coupling are assumed to have the same order of magnitude, so that the two phase transitions can affect each other. It is found that the coupling may make the two phase transitions take place simultaneously if the uncoupled FOPT occurs prior to the uncoupled SOPT with compression. In the opposite case, the coupling will make the FOPT take place at a lower pressure, even still behind the SOPT. In both cases, the gas-liquid phase separation always leads to a decrease in the averaged order parameter of the orientational phase transition. The theoretical result in the former case is qualitatively consistent with experimental data.

II. MODEL

We first consider the gas-liquid phase transition on a Langmuir monolayer. Such a FOPT can be described by a position-dependent order parameter: $C(\mathbf{x}) \sim [A(\mathbf{x}) - A_g]/A_g$, where $A(\mathbf{x})$ is the area occupied by a molecule at $\mathbf{x}$ and A_g is the averaged area of the gas molecules in the gas-liquid coexistence. The (Gibbs) free-energy density for the FOPT is given by [5,9]

$$f_c[\{C(\mathbf{x})\}] = \frac{1}{2}\kappa_1[\nabla C(\mathbf{x})]^2 + f_1\left[\eta C(\mathbf{x}) + \frac{1}{4}C^2(\mathbf{x}) + \frac{1}{2}C^3(\mathbf{x}) + \frac{1}{4}C^4(\mathbf{x})\right]. \tag{1}$$

Here f_1 and κ_1 are positive constants. $\eta = (P-P_0)/P_0$ with P_0 the pressure of the two-phase coexistence. The gradient term provides a positive energy at interfaces between gas and liquid phases, and so it is unfavorable to a phase separation. In the absence of the gradient term, the free energy f_c given in Eq. (1) exhibits two minima at $C=0$ and $C=-1$ at $\eta=0$, respectively, corresponding to the gaseous phase and liquid phase. In this case, as soon as the gas-molecule area is decreased to A_g by compression, the liquid nucleus would begin to form inside the gaseous phase. If η is nonzero, the locations of the minima are shifted and there is no longer degeneracy in the free energy. For $\eta<0 (P<P_0)$, the free energy for $C>0 (A>A_g)$ is lower and so only the gaseous phase is stable, while for $\eta>0 (P>P_0)$, only the liquid phase is stable.

Second, we consider the orientational phase transition of the rodlike molecules on the Langmuir monolayer. The local coarse-grained order parameter is given by $S(\mathbf{x}) = \cos\theta$, where θ is the tilt angle of the rodlike dipolar molecules at $\mathbf{x}$ away from the normal direction of the monolayer. The free-energy density of this SOPT alone is expressed as

$$f_s[\{S(\mathbf{x})\}] = \frac{1}{2}\kappa_2[\nabla S(\mathbf{x})]^2 + f_2[r_s S^2(\mathbf{x}) + \beta S^4(\mathbf{x})]. \tag{2}$$

Here f_2, κ_2, and β are also positive constants, and $r_s = (P_s - P)/P_0$, where P_s is the pressure at the SOPT point. For $P<P_s$ ($r_s>0$), all the molecules lie on the water surface so that the polar order parameter always equals zero. For $P>P_s$, ($r_s<0$), we have $S=\sqrt{-r_s/2\beta}$, indicating that the molecular orientation has a component in the normal direction of the water surface. Unlike in Ref. [5] where $P_s=P_0$ was assumed, in this work we will study the most general cases of $P_s>P_0$ and $P_s<P_0$.

The next step is to model the coupling between the FOPT and SOPT. The simplest coupling complying with symmetry requirements gives the following free-energy density

$$f_{cs}[\{C(\mathbf{x})\},\{S(\mathbf{x})\}] = f_2 g C(\mathbf{x}) S^2(\mathbf{x}), \tag{3}$$

where g is the coupling constant. In the liquid phase where $C(\mathbf{x})=-1$, high molecular density and steric repulsive interactions among molecules [4] make the rodlike molecules tilt up along the normal direction of the monolayer, yielding $S(\mathbf{x})>0$, while in the gaseous phase where $C(\mathbf{x})=0$, the steric repulsive interactions can be neglected for low molecular density so that $S(\mathbf{x})=0$. In order to describe this physical phenomenon, g must be taken positive so that the coupled free-energy is lower for the collocation of $C(\mathbf{x})=-1$ with $S(\mathbf{x})=1$. Evidently, a negative g would yield an unphysical result.

We employ the Langevin equations to calculate equilibrium distributions of C and S. As C is assumed to be conserved and S to be nonconserved, the Langevin equations for C and S are given by [5,9,10]

$$\frac{\partial C}{\partial t} = D\nabla^2 \frac{\delta F(\{C\},\{S\})}{\delta C}, \tag{4}$$

$$\frac{\partial S}{\partial t} = -\lambda \frac{\delta F(\{C\},\{S\})}{\delta S}, \tag{5}$$

where $F = \int (f_c[\{C(\mathbf{x})\}] + f_s[\{S(\mathbf{x})\}] + f_{cs}[\{C(\mathbf{x})\},\{S(\mathbf{x})\}]) d\mathbf{x}$ is the total free energy. Consider a two-dimensional lattice of 50×50 with periodic boundary conditions. We solve numerically Eqs. (4) and (5) by using a finite-difference scheme in both time and space, and simulate spatial equilibrium distributions of the two order parameters C and S. The liquid nucleus is assumed to form first at the center of the lattice. It has been checked that the choice of the initial condition does not affect the present numerical results.

III. CASE OF $P_0<P_S$

We first discuss the case where in the absence of coupling between the two phase transitions, the FOPT occurs prior to the SOPT with compressing molecular area. In reality, the coupled effects play an important role in the two phase transitions. In the total free-energy density, the prefactor of term $S^2(\mathbf{x})$ can be written as

$$r_s'(\mathbf{x}) = gC(\mathbf{x}) + \delta - \eta, \tag{6}$$

where we have replaced r_s by $\delta-\eta$ with $\delta = (P_s - P_0)/P_0$, introduced to indicate the difference between the phase transition points of FOPT and SOPT. In a pure gaseous state, $C(\mathbf{x})=0$ and so $r_s' = r_s$. As soon as the gas-liquid phase transition occurs at $\eta=0$, $C(\mathbf{x})$ at the liquid nucleus changes from 0 to -1, where there will be a reverse in sign of r_s' provided $\delta<g$. As a result, as long as the difference between P_s and P_0 is not big, the coupling between FOPT and SOPT will make the two phase transitions take place simulta-

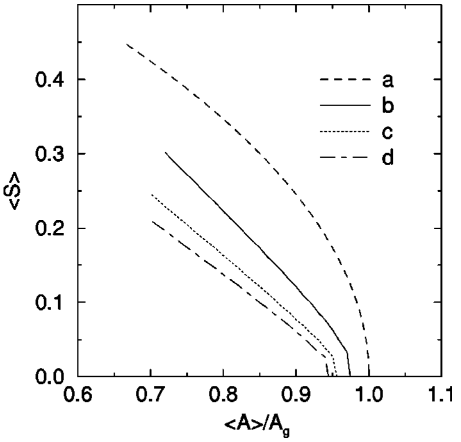

FIG. 1. $\langle S\rangle$ as a function of $\langle A\rangle/A_g$ for several values of g and C_0: (a) $g=0$ and $\delta=0$, (b) $g=1$ and $\delta=0.25$, (c) $g=1$ and $\delta=0.5$; (d) $g=0.5$ and $\delta=0.25$.

neously. This conclusion is consistent with the real physical process. In the liquid phase, the molecular density is high, and strong steric repulsive interactions among molecules always lead to $S(\mathbf{x})>0$ [4]. As a result, as soon as the FOPT occurs due to compression, finite orientational order parameters appear, the coupling making the orientational phase transition take place in advance.

Figure 1 shows calculated results for the spatial average of $S(\mathbf{x})$ as a function of the averaged molecular area for several different δ and g. Here we take $f_1=2f_2=20$, $\kappa_1=\kappa_2=5$, and $\lambda=D=1$. Since f_1 and f_2 are taken of the same order of magnitude, the FOPT and SOPT have effects on each other. Owing to the coupling (nonzero g), $\langle S\rangle$ exhibits approximately linear dependence on $\langle A\rangle$, as shown by the lower three curves in Fig. 1. They are quite different from the upmost curve for $\langle S\rangle$ versus $\langle A\rangle$. The latter corresponds to an orientational phase transition taking place independently at $A=A_g$, with $g=0$ and $\delta=0$ taken. The difference between them can be understood by the following argument. After the gas-liquid phase transition occurs, the orientational order parameters S_l in the liquid phase and S_g in the gaseous phase remain unchanged. Since $S_g=0$, the increase of $\langle S\rangle$ depends mainly on the increase of the area fraction of the liquid phase with compression, i.e.,

$$\langle S\rangle=yS_l+(1-y)S_g, \tag{7}$$

where y is the area fraction of the liquid phase and governed by the usual lever rule. On the other hand, the averaged area per molecule is given by

$$\langle A\rangle=yA_l+(1-y)A_g, \tag{8}$$

where A_l is the molecular area of the liquid phase in the gas-liquid coexistence. Combining Eqs. (7) and (8), one gets linear dependence of $\langle S\rangle$ on $\langle A\rangle$. In reality, the mean area of the gaseous molecules is rather large compared with that of the liquid molecules ($A_g \gg A_l$) and $S_g=0$, so that $\langle A\rangle=S_l(1-\langle A\rangle/A_g)$. Replacing r_s in Eq. (2) by r_s' given in Eq. (6), we have

$$S^2(\mathbf{x})=\frac{\eta-gC(\mathbf{x})-\delta}{2\beta}. \tag{9}$$

Since $C(\mathbf{x})$ is negative in the liquid region, a bigger g or a smaller δ yields a larger value of S_l, resulting in a larger slope of the $\langle S\rangle$ versus $\langle A\rangle$ line.

It is also shown in Fig. 1 that the common phase-transition point of the FOPT and SOPT is always at A slightly lower than A_g. It arises from the existence of the gradient term that provides a positive interfacial energy and so is unfavorable to the spatial phase separation. As A is decreased to A_g, the liquid nucleus cannot form until a decrease in energy due to gas-liquid phase separation exceeds an increase of the interfacial energy. As a result, the gas-liquid transition is shifted down to $A<A_g$, at which the area fraction of the liquid phase will have a small uncontinuous jump. However, this effect is size dependent, decreasing with increasing the size of the system. In the thermodynamic limit, where the system size goes to infinity, the interfacial effect can be neglected and the shift in the phase transition vanishes. On the other hand, the coupled free energy given in Eq. (3) is favorable to the formation of the liquid nucleus, because it can provide a negative free energy for $C(\mathbf{x})=-1$. Thus, a larger value of g will lead to a bigger right-shift of the phase-transition point. On the other hand, as soon as the liquid nucleus is formed, $C(\mathbf{x})=-1$ at it gives rise to a finite S_l according to Eq. (9). It follows from Eq. (7) that the jump in $\langle S\rangle$ at the phase-transition point comes from a sudden appearance of nonzero S_l and y. The greater g and the less δ, the greater S_l becomes, $\langle S\rangle$ exhibiting a bigger jump. All the arguments above are suitable to the case of $\delta<g$ and consistent with the calculated results shown in Fig. 1. If δ is larger than $g|C(\mathbf{x})|$ in the liquid region, according to Eq. (9), S_l is still equal to zero after the gas-liquid phase transition has taken place. In this case, f_{cs} is always equal to zero and the coupling has little effect on the orientational phase transition.

IV. CASE OF $P_0>P_S$

We now discuss the opposite case in which the uncoupled SOPT occurs prior to the FOPT. $\delta=(P_s-P_0)/P_0$ still indicates the distance between two uncoupled phase transition points, but $\delta<0$ due to $P_s<P_0$. In the total free energy, the renormalized prefactor of $C(\mathbf{x})$ is given by

$$\eta'(\mathbf{x})=\eta+\alpha gS^2(\mathbf{x})=\frac{P}{P_0}-[1-\alpha gS^2(\mathbf{x})], \tag{10}$$

where $\alpha=f_2/f_1$. At the SOPT point where $P=P_s<P_0$ and $S=0$, η is always negative and the gas-liquid phase transtion is not able to take place. By decreasing the molecular area by compression, S in the uniform gaseous state increases gradually. As S is increased to a critical value, η' can change its sign from negative to positive and so the gas-liquid phase transition occurs at $P=P_0(1-\alpha gS^2)$. In this case, the FOPT point shifts below P_0 but above P_s.

Figure 2 shows the calculated result for $\langle S\rangle$ as a function of $\langle A\rangle$ for different g and δ, where $f_1=f_2=20$ $(\alpha=1)$ and the other constant parameters are the same as in Fig. 1. For ease of comparison, the upmost curve is plotted corresponding to the uncoupled SOPT of $g=0$. It is found that as soon as the FOPT takes place, $\langle S\rangle$ first exhibits a small drop and then increases linearly with the decrease of $\langle A\rangle$. From Eq.

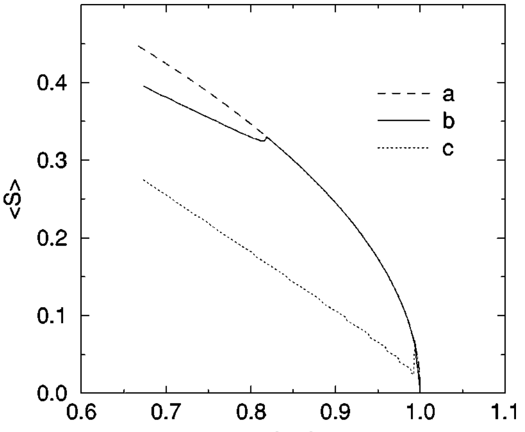

FIG. 2. $\langle S\rangle$ as a function of $\langle A\rangle/A_s$ (A_s being the molecular area corresponding to P_s, where the SOPT occurs) for several values of g and δ: (a) $g=0$, (b) $g=1$ and $\delta=-0.5$, (c) $g=2$ and $\delta=-0.5$.

(10) as well as Fig. 2, one finds that the coupled effect of the SOPT on the FOPT is governed by the coupling strength. The larger αg, the earlier the FOPT takes place. The linear dependence of $\langle S\rangle$ on $\langle A\rangle$ can be understood by Eqs. (7) and (8) as well as the same argument as in the case of $P_0<P_s$. It arises from the fact that both $\langle S\rangle$ and $\langle A\rangle$ are proportional to y. During the gas-liquid phase transition process, the order parameters S_l and S_g remain unchanged, as shown in Fig. 3.

Analogous to the jump in $\langle S\rangle$ in Fig. 1, the drop in $\langle S\rangle$ in Fig. 2 is also related to the presence of the gradient terms in the free energy. A positive interfacial energy makes the critical pressure, at which the real FOPT takes place, higher than $P_0(1-gS^2)$. As soon as the FOPT occurs, there is a sudden increase in y, resulting in a sudden increase in A_g and a sudden decrease in S_g. At this very moment, the change of $\langle S\rangle$ is given by

$$\Delta\langle S\rangle=\Delta y(S_l-S_g)+\Delta S_g, \tag{11}$$

where ΔS_g is the difference between the orientational order parameters in the gaseous region after the gas-liquid phase transition takes place and in a pure gaseous state. It is found from Fig. 3 that the former is smaller than the latter, and so ΔS_g is negative. Even though $S_l-S_g>\Delta S_g$ shown in Fig. 3, a very small Δy may yield a negative $\Delta\langle S\rangle$ or a drop in $\langle S\rangle$.

Another feature shown in Fig. 3 is that $C_l<-1$ in the liquid region and $C_g>0$ in the gaseous region. It is quite different from an uncoupled gas-liquid phase transition at $P=P_0$, where $C_l=-1$ and $C_g=0$. In reality, $C_l<-1$ indicates that the molecular density in the liquid region is greater than that of $C_l=-1$ and $C_g>0$ indicates that the molecular density in the gaseous region is less than that of $C_g=0$. This is because the coupling of the orientational phase transition shifts the FOPT to a lower pressure $P_0(1-gS^2)$, at which the mean area of the gas molecules must be larger than A_g.

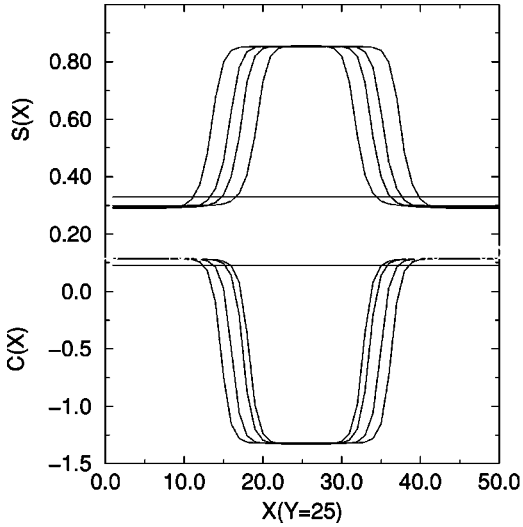

FIG. 3. Evolution of $C(\mathbf{x})$ and $S(\mathbf{x})$ with the growth of a liquid nucleus inside the gaseous phase, where $g=1$ and $\delta=-0.5$. This is a cross section at $Y=25$ of a 50×50 grid with $\langle A\rangle/A_s$ taken to be 0.80, 0.77, 0.73, and 0.70, respectively. The horizontal lines denote uniform S and C just before the FOPT occurs.

The present result can be understood by analogy with the P-V phase diagram in a three-dimensional gas-liquid phase transition, where the lower the pressure, the wider the gas-liquid coexistent region, having a larger molecular volume of gas and a smaller mole volume of liquid. We wish to point out that in the present case there are orientational order parameters S_l and S_g in the liquid and gaseous regions, respectively, both of them having finite values $(S_l>S_g>0)$. Such a phase separation differs from that in the case of $P_0<P_s$, where there is only nonzero S_l in the liquid region and $S_g=0$ in the gaseous region.

V. SUMMARY

In summary, as an example of coupled gas-liquid and orientational phase transitions, we have studied the coupled effects between a FOPT and a SOPT. It is shown that if the FOPT occurs prior to the SOPT with compression, a strong enough coupling ($g>\delta$) can make the two phase transitions occur at the same time. In the opposite case of the SOPT occuring prior to the FOPT, the coupling shifts the FOPT to taking place at a lower pressure $(P_0>P>P_s)$. In both cases, the coupling always results in a decrease of the averaged orientaional order parameter. The present theory has been compared with experimental results for the orientational order parameter in a Langmuir monolayer, a qualitative agreement between them being obtained in the case of $P_s>P_0$ and $g>\delta$.

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