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Possible observation of surface and special transitions in mixtures

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We point out a possible mechanism for physically realizing surface and special (or surface-bulk) transitions in binary mixtures. Impurities which affect the critical temperature may interact with the wall and thus enhance the effective interaction of the components in its vicinity. The same mechanism applies to the already observed superfluid film formation near a wall in ^{3}He-^{4}He mixtures, in the proximity of the λ line.

I. INTRODUCTION

Phase-transition phenomena which take place near a free surface or a wall have recently become the object of considerable interest.[1] Some such phenomena are due to symmetry breaking induced by the wall; this is, e.g., the case of critical adsorption,[2] wetting,[3] layering,[4] and surface-induced disorder.[5] Other effects are related to spontaneous symmetry breaking near the surface. These particular phenomena were studied by Binder and Hohenberg,[6] and by Lubensky and Rubin,[7] who identified the different transitions and constructed the corresponding phase diagram.

The effective ordering interactions near the wall are, in general, different from that in the bulk. This is represented by a surface-decoupling parameter c. *Positive* c corresponds to surface interactions which are *weaker* than in the bulk; this is the usual case, since the molecules near the wall do not have neighbors on the other side. The ordering transition on the surface is then only due to the ordering in the bulk, and is called the *ordinary* transition. It has been extensively studied in mean-field and renormalization-group treatments.[8] A few superlative experiments measured the characteristic surface exponent β_1 near this transition.[9]

The case of *negative* c corresponds to surface interactions which are *stronger* than in the bulk. This opens the way to the interesting possibility that order may appear near the surface at higher temperatures than in the bulk. This transition is called *surface* transition by Lubensky and Rubin.[9] As the temperature is lowered towards the bulk critical temperature T_c, the order progressively propagates into the bulk. The transition at T_c is called the *extraordinary* transition. The limiting case $c=0$ corresponds to a multicritical point called the *special* (or surface-bulk) transition; some theoretical studies consider this unusual phenomenon.[10] Figure 1 represents a schematic phase diagram in the $(c, T-T_c)$ plane.

No real physical systems have been considered, to our knowledge, as belonging to the $c<0$ case. We wish to point out in this paper the possibility of *physically* realizing this case in fluids by means of a mechanism based on impurities. Let us consider, e.g., a binary mixture near its consolute point. The critical temperature can be increased by adding a small concentration of impurities to the mixture.[11] If these impurities experience a preferential attraction to the wall, the first few layers of fluid will have a tendency to undergo the transition at higher temperatures than if they were in the bulk. This may open the way to a surface transition. Varying the concentration of impurities allows one to tune the surface parameter c, and therefore to also observe the special transition.

An analogous phenomena was in fact observed in ^{3}He-^{4}He mixtures.[12–16] It concerns the onset of *superfluid* ordering near the wall, where ^{3}He concentration is lower. Here the λ temperature is a decreasing function of the concentration of ^{3}He, which on the other hand experiences an effective repulsion from the wall due to zero-point

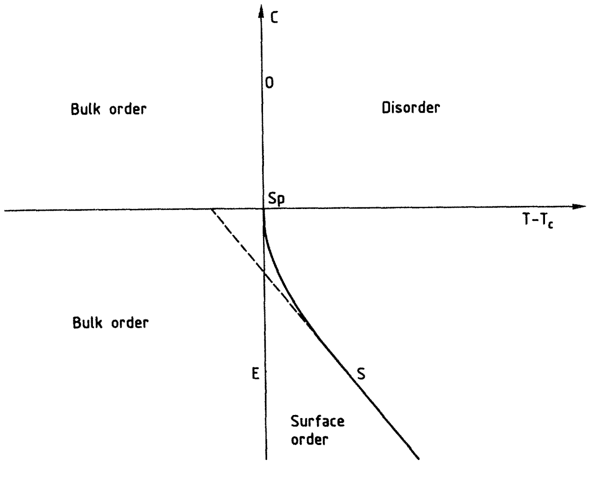

FIG. 1. Schematic phase diagram of surface phase transitions in the $T-T_c$ c plane after Lubensky and Rubin (Ref. 7). Solid lines represent, respectively, the ordinary (O), surface (S), and extraordinary (E) transitions. Dashed line represents the critical temperature for a two-dimensional system with interaction $J(1+D)$. Position of the special transition is identified by Sp.

motion effects. One observes, therefore, superfluid film formation near the wall. One can explain this by different phenomenological models, such as the local-continuum model of Ref. 17. We interpret this phenomenon as a surface transition. The peculiarities of superfluid ordering in two dimensions make this phenomenon more delicate to investigate in detail. Our interpretation, however, enables us to obtain new predictions on the behavior of superfluid ordering near the wall.

We first review the usual theory of surface and special transitions, and show how one can tune the surface-decoupling parameter c by introducing impurities. We point out the conditions to be satisfied so that this mechanism leads to interesting experimental consequences. We then discuss the available experimental data on the superfluid film formation in ^{3}He-^{4}He mixtures, and sketch how the scheme we propose must be adapted to this case. We finally review the most interesting experimental consequences of our proposal.

II. SURFACE AND SPECIAL TRANSITIONS

Phase-transition phenomena near a wall are best discussed in the scheme of semi-infinite models. For the case of a scalar-order parameter it is convenient to consider a semi-infinite Ising model described by the Hamiltonian

$$H=-\sum_{\langle ij\rangle}J_{ij}S_iS_j-\sum_i h_iS_i,\quad S_i=\pm 1 \tag{1}$$

where i,j are points in a simple semi-infinite cubic lattice contained in the $z\geq 0$ half-space. The first sum runs only over nearest-neighbor lattice points. The *surface* S is defined as the set of lattice points belonging to the $z=0$ plane. The remaining points define the *bulk* B. We choose the couplings J,h, appearing in (1), as follows:

$$J_{ij}=\begin{cases}J(1+D), & \text{if } i \text{ and } j \text{ belong to } S\\ J \text{ otherwise}\end{cases} \tag{2}$$

$$h_i=\begin{cases}h_1 & \text{if } i \text{ belongs to } S\\ h & \text{otherwise}\ .\end{cases} \tag{3}$$

We shall consider the case of neutral wall ($h_1=0$), and we set, furthermore, $h=0$. A molecular-field analysis of this model[7] leads to the phase diagram presented in Fig. 1, with a surface-decoupling parameter c related to D by

$$c=1-4D\ . \tag{4}$$

Renormalization-group calculations[8,10] confirm the qualitative features of this diagram and identify each transition by a corresponding fixed point.

The *ordinary* transition (O) corresponds to spontaneous ordering in the bulk. It is described by a renormalization-group fixed point where $c\to\infty$. The surface decoupling appears, therefore, as an irrelevant parameter (the relevant ones being $t=T-T_c/T_c$, h, and the surface field h_1). The scaling form of the order-parameter profile (at $h_1=0$, $T<T_c$) is simply given by

$$m(z;t)=z^{-\beta/\nu}M_0(z/\xi)\ . \tag{5}$$

where ξ is the bulk coherence length.

The *surface* transition (S) corresponds to ordering taking place near the surface, and is described by the same fixed point as a usual transition in *two* dimensions. The relevant parameter of this transtion is $t_1=T-T_c^s/T_c^s$, where T_c^s is the surface transition temperature (and possibly the surface field h_1). Thermodynamical quantities obey usual scaling laws with respect to these variables as in ordinary *two*-dimensional systems. One sees in Fig. 1 that the line of surface transitions tends to coincide with the line of transition of a two-dimensional model with coupling equal to $J(1+D)$ (dashed line) when D becomes sufficiently large.

As we lower the temperature towards the bulk critical temperature, keeping c fixed, the order propagates from the surface into the bulk. One reaches thus, the *extraordinary* transition (E). Its nature is still the object of controversy.[18] It is not, however, our purpose to discuss the properties of this transition.

The lines where all these transitions take place meet at the ($c=0,T=T_c$) point, which corresponds to the *special* transition (Sp) (also called the surface-bulk transition). Around this point both c and t (as well as the symmetry-breaking fields h,h_1) are relevant. The scaling form of the order-parameter profile is

$$m(z;t,c)=z^{-\beta/\nu}M_s(z/\xi;c/t^{\phi_s})\ , \tag{6}$$

where the *crossover exponent* ϕ_s, computed by a two-loop ϵ expansion, is estimated to be[10] 0.68. Note that the scaling form,[6] as such, does not give the small z behavior of the profile, for which it is necessary to know the behavior of the function M_s. This can be obtained via a short-distance expansion.[19] One can compute explicitly the scaling function M_s in the ϵ expansion as a function of z and c (and h_1).[19]

Within this scheme one obtains the behavior of the surface transition line near the special transition,

$$T_c^s-T_c\propto c^{1/\phi_s}\ . \tag{7}$$

It follow from Eqs. (6) and (7) that the ordered region just below the surface transition temperature extends over a layer of thickness proportional to the bulk coherence length ξ—a length which diverges as the special transition is approached.

This phase diagram—and the corresponding scaling laws—have so far been the object of purely theoretical investigation due to the impossibility of tuning the surface-decoupling parameter c. In the systems where surface critical effects were investigated experimentally,[2,9] c appeared to be positive and large [when no special effects enhance interactions on the surface, the effective interactions near it are weaker due to the semi-infinite geometry, cf. Eq. (4)]. Experimental investigations were therefore limited to the ordinary transition.

Now we shall see how, by introducing a small concentration x of impurities which interact with the wall, one can tune the (effective) parameter c, and thus explore the wide phase diagram. Let us consider, e.g., a binary mixture with a small concentration of impurities. One knows that their presence can strongly affect the critical temperature.[20] Suppose now that the added impurities strongly interact with the wall (contrary to the components of the mixture).[21] The concentration of impurities near the wall will be, therefore, different from the bulk. If the critical temperature increases with the impurity concentration, and this concentration is higher near the wall, then one may reach a situation in which the transition takes place near the wall at higher temperatures than in the bulk.

These arguments are confirmed by a molecular-field calculation on a lattice model of a binary mixture with impurities, the Blume-Emery-Griffiths[22] model, which is defined by the Hamiltonian

$$H=-\sum_{\langle ij\rangle}(J_{ij}S_iS_j+K_{ij}S_i^2S_j^2)-\sum_{i}(h_iS_i-\Delta_iS_i^2)\,,\qquad S_i=0,\pm 1\,. \tag{8}$$

Positive or negative spin represent here the presence of one or the other component of the binary mixture; zero spin represents the presence of an impurity. The "magnetic" field h and the "crystalline" field Δ are, respectively, related to the chemical potential of the components of the mixture and the impurities. We assume J_{ij} as in Eq. (2), $h_i=0$ as before, and a Δ_i which is *lower* on the surface than in the bulk, representing an effective *repulsion* of impurities from the wall;

$$\Delta_i=\begin{cases}\Delta_1, & \text{if } i \text{ belongs to } S,\\ \Delta>\Delta_1, & \text{otherwise}\end{cases}\;. \tag{9}$$

The calculation is highly simplified if one assumes $K_{ij}=0$, what is known as the Blume-Capel[23] limit. One then obtains a line of critical points for the bulk, whose temperature $T_c(x)$ is a *decreasing* function of the bulk impurity concentration x. Near this line the molecular-field equations for the order-parameter profile reduce to those of a semi-infinite Ising model, provided the correct distance from the critical temperature is considered, and an *effective* c parameter is introduced, which is given by

$$c_{\text{eff}}=c-6x(1-e^{-\phi/kT})-6[1-x(1-e^{-\phi/kT})]\times\left[\frac{T}{T_c(x)}-1\right], \tag{10}$$

where $\phi=\Delta_1-\Delta$ and the "bare" c parameter is given by Eq. (4). One sees, therefore, that by changing the impurity concentration x (and therefore both Δ and Δ_1) one may make the effective c parameter vanish or even become negative at the bulk transition temperature $T_c(x)$. One may therefore obtain a line of surface transitions and a special transition point. Below the surface transition line one obtains a nontrivial order-parameter profile, which in turn induces an impurity-concentration profile. If $K_{ij}\neq 0$ the molecular-field equations for the order parameter and the impurity concentration couple and their solution becomes more complex, but the solution maintains the same qualitative features. We conjecture, therefore, that the semi-infinite Ising model and the semi-infinite Blume-Emery-Griffiths model (above the tricritical point) belong to the same universality class. This conjecture may be tested by real-space renormalization-group methods.

We now summarize the necessary conditions for experimentally exploiting this effect. It is important to realize a wall which interacts almost symmetrically with the two components of the mixture ($h_1\simeq 0$). This may be achieved either by a careful choice of the components[24] or by coating the wall with some material (this also opens the possibility of varying h_1 at will). It is then necessary that the impurities strongly increase (decrease) the critical temperature[11] and are strongly attracted (repelled) by the wall, with respect to the other components. The choice of a system where Fisher's exponent renormalization is not observed should make the interpretation of the data easier.

III. SUPERFLUID FILM FORMATION IN ^{3}He-^{4}He MIXTURES

Our point of view is corroborated by the experimental observations of an analogous phenomenon: superfluid film formation near the walls in ^{3}He-^{4}He mixtures. The ^{3}He atoms play the role of inert impurities for the λ transition experienced by ^{4}He atoms. The van der Waals attraction by the wall is the same for the two isotopes. (The van der Waals attraction is so strong, that helium actually forms a thin *solid* layer attached to the wall.) Nevertheless the difference in their zero-point motion leads to a difference in their effective atomic volumes, ^{4}He being "smaller" than ^{3}He by about 32%. This effect leads to a preferential attraction of ^{4}He atoms towards the wall. (It has been analyzed by Laheurte in Ref. 13.)

Superfluid film formation was first investigated by Keyston and Laheurte more than fifteen years ago.[12] In this and in the subsequent experiments[13] the authors observed the heat leaks due to film flow in the region of high-^{3}He concentration, and therefore near the phase separation line.

Several authors[14–16] extended these experiments to the vicinity of the λ line. Various observations were used to locate the superfluid film formation: (a) the onset of superflow through a Vycor superleak[14,22]; (b) the increase in heater power needed to stabilize temperature[15]; (c) the dielectric constant anomaly measured by capacitive methods[15,16]; (d) the anomaly in the thermal diffusion ratio and in the thermal conductivity.[16] All these methods agree in the localization of the line of superfluid film formation; a line which meets the λ line at about $T=1.2$ K, the ^{3}He molar concentration being about 0.54. The available experimental points near the λ line are shown in Fig. 2. This diagram is the analog of the one shown in Fig. 1; the λ line corresponds to the ordinary-extraordinary transition line, whereas the line of superfluid film formation corresponds to the surface transition line. The mechanism we have described in the context of binary mixtures with impurities applies, therefore, also to ^{3}He-^{4}He mixtures, with the ^{4}He atoms playing the role of the "active" components, and the ^{3}He atoms that of the impurities, at least in proximity of the λ line.

There is, however, an important difference in the helium mixture case, since the Mermin-Wagner-Hohenberg theorem[25] implies that the superfluid *order parameter* is zero even below the superfluid film formation line. The surface transition line is, therefore, of the Kosterlitz-Thouless type.[26] This is likely to affect the behavior at the extraordinary transition. We expect on the contrary,

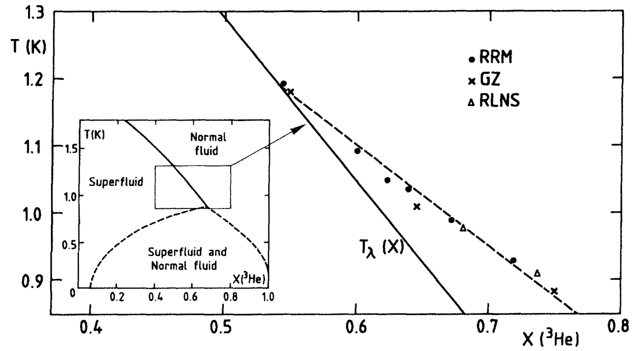

FIG. 2. Line of superfluid film formation near the λ line in ^{3}He-^{4}He mixtures, after the observations of Ruppeiner, Ryschkewitsch, and Meyer (Ref. 16) (RRM), of Gearhardt and Zimmermann (Ref. 14) (GZ), and of Romagnan, Laheurte, Noiray, and Saam (Ref. 15) (RLNS).

that the scaling form (6) near the special transition will continue to hold. Quantitative support of this idea can be obtained by considering the generalized Blume-Emery-Griffiths model with a vector order parameter.[27] This may be analyzed by means of Migdal-Kadanoff real-space renormalization scheme. This will be the object of further work.

A direct consequence of our point of view which should be experimentally testable is that the superfluid film (the region near the wall where the superfluid *density* is nonzero) just below the superfluid film formation line should become thicker as one approaches the special transition, as already remarked in Ref. 17. Eventually its thickness will largely exceed the thickness of the region where the wall attractions strongly modify the concentration of ^{4}He atoms. It would be, therefore, interesting to measure and compare these thicknesses.

IV. CONCLUSIONS

The impurity-driven mechanism described in this paper can allow one to tune the effective surface-decoupling parameter, bringing special and surface transitions in evidence. Since the surface field h_1 can, in principle, be easily tuned (e.g., by coating), one has the possibility of exploring the whole phase diagram of transitions near a surface.

The observed superfluid film formation near a wall in ^{3}He-^{4}He mixtures appears as a surface (or special) transition. Besides the behavior of the superfluid film thickness we pointed out before, this implies that the transition line should approach the λ line according to the behavior given in Eq. (7), i.e., with an exponent larger than 1. It should be interesting to approach the special transition point sufficiently close to observe this behavior.

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