Wetting transition for the contact line and Antonov's rule for the line tension

A. Robledo and C. Varea
Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, México 01000, Distrito Federal, Mexico

J. O. Indekeu
Laboratorium voor Vaste Stof-Fysika en Magnetisme, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium
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The standard wetting transition consists of the transformation of a microscopically thin two-dimensional interface into a macroscopically thick structure composed of two interfaces separated by a bulk phase. We consider the one-dimensional analog of this phenomenon, when a contact line among three or more phases decomposes into two contact lines separated by an interface. We uncover a wetting transition for the contact line, which occurs at *surface* two-phase coexistence, as a function of a line or edge field. This is exemplified by means of a lattice mean-field calculation for an Ising model bounded by two surfaces that meet in an edge.

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I. INTRODUCTION

The contact line, also referred to as the three-phase line, is the macroscopic one-dimensional locus at which three phases, say, α, β, and γ, and three interfaces, $\alpha\beta$, $\beta\gamma$, and $\alpha\gamma$, meet [1]. This type of equilibrium inhomogeneity, more complex than those that give rise to two-dimensional interfaces, has attracted attention recently [2–6], and some properties of its excess free energy per unit length, or line tension τ, have been analyzed. An interesting question is the fate of τ at the wetting transition since there the contact line disappears. Phenomenological studies have probed into this problem, and preliminary evidence was gathered for the vanishing of τ at a first-order wetting transition [2]. However, recent work along these lines suggests that τ may behave very differently and may occasionally show a divergence upon approach to such wetting transition [3,4]. Most, if not all, works that have dealt with this question to date are concerned with mean-field theories (continuum or lattice based). The presumably important effects of fluctuations on the line tension have not yet been addressed systematically.

Another compelling question concerns the behavior of the line tension associated with surface critical phenomena. The critical exponents that describe the vanishing of τ at surface criticality (specifically, at the ordinary, extraordinary, special, and pure surface transitions [7,8]) have been identified using mean-field theory and scaling arguments [6].

The macroscopic condition for the existence of a three-phase line is easily visualized in terms of the Neumann triangle construction [1]. There, the three tensions σ_{ij}, with $i,j=\alpha$, β, and γ, associated to the three possible interfaces are related to the sides of the Neumann triangle and the dihedral angles occupied by the three phases to the angles of the triangle. In the well-known case that one of the phases is an undeformable solid with a planar surface, the Neumann triangle description reduces to Young's law, $\sigma_{\alpha\gamma}=\sigma_{\beta\gamma}+\sigma_{\alpha\beta}\cos\theta$, with θ the pertinent contact angle. The Neumann triangle collapses into a line when the largest of the three tensions, say, $\sigma_{\alpha\gamma}$, is equal to the sum of the other two. Then, the equilibrium configuration of the three phases is that in which the β phase completely wets the interface between the α and the γ phases. The wetting condition among the three surface tensions is known as Antonov's rule [1], $\sigma_{\alpha\gamma}=\sigma_{\alpha\beta}+\sigma_{\beta\gamma}$, and when it is satisfied, the three-phase contact line disappears. Since 1977, it is known that a *wetting phase transition* marks the onset of the complete wetting regime, precisely at the instance where Young's law becomes Antonov's rule [9,10].

A more complex situation arises when four phases α, β, γ, and δ are in thermodynamic equilibrium, as is the case of the two droplets (of two immiscible liquids) in Fig. 1, resting on a substrate and in contact with air. There

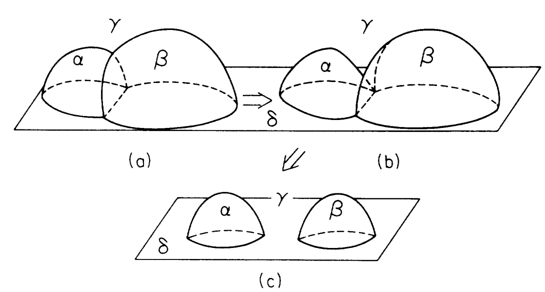

FIG. 1. Two immiscible liquid drops (phases α and β) resting on a substrate (phase δ) and in contact with air (phase γ). In (a) all surface tensions produce nonzero dihedral angles, and four lines and two points of tension are formed. In (b) a wetting transition has occurred at the $\alpha\beta$ interface and air intrudes between the two droplets, drying the two liquids, and three line tensions persist. In (c) a wetting transition has taken place at the $\alpha\beta\gamma\delta$ contact line, and the two drops no longer appear to be in contact.

are now six different possible interfaces and four possible lines of three-phase contact. When the γ phase (say, air in Fig. 1) wets, or, perhaps more appropriately "dries," the $\alpha\beta$ interface (in Fig. 1 that interface where the two liquid droplets touch each other), only three possible lines of multiple-phase contact may subsist, namely, two three-phase contact lines, those at the $\alpha\gamma\delta$ and $\beta\gamma\delta$ intersections, and the new four-phase contact line $\alpha\beta\gamma\delta$. It is interesting to contemplate the structure of the $\alpha\beta\gamma\delta$ line [11]. There are two physically distinct cases. One corresponds to genuine four-phase contact along a microscopically thin line [Fig. 1(b)]. The other shows two separate three-phase contact lines into which the four-phase contact line has dissociated [Fig. 1(c)]. Note the analogy with the wetting or "unbinding" transition at interfaces.

Which of the two states, microscopically "thin" or macroscopically "thick," of the $\alpha\beta\gamma\delta$ line is realized depends on the relative values of the three line tensions $\tau_{\alpha\beta\gamma\delta}$, $\tau_{\alpha\gamma\delta}$, and $\tau_{\beta\gamma\delta}$. In analogy with ordinary wetting phenomena at surfaces, when, say, $\tau_{\alpha\beta\gamma\delta} < \tau_{\alpha\gamma\delta} + \tau_{\beta\gamma\delta}$, the equilibrium configuration of the system is that of a "thin" $\alpha\beta\gamma\delta$ line. Furthermore, a point inhomogeneity (with its corresponding excess free energy or point tension) appears at the intersection of the $\alpha\beta\gamma\delta$, $\beta\gamma\delta$, and $\alpha\gamma\delta$ lines [Fig. 1(b)]. On the other hand, when $\tau_{\alpha\beta\gamma\delta} = \tau_{\alpha\gamma\delta} + \tau_{\beta\gamma\delta}$, i.e., when "Antonov's rule" for the line tension holds, the equilibrium configuration of the system is that of the "thick" $\alpha\beta\gamma\delta$ line, and the two droplets appear to be no longer in contact. Therefore, the balance among excess free energies due to different configurations of *line* inhomogeneities, although small, may determine the macroscopic geometry of three-dimensional systems. Of course, in general, different configurations will correspond to different excess *surface* free energies as well. However, in some simplified geometries, the idealized argument that we have proposed is exactly applicable. Indeed, a simple model with which we will exemplify the above-described behavior is a spin-$\frac{1}{2}$ Ising model with an edge inhomogeneity formed by two perpendicular surfaces, that is undergoing a first-order wetting transition.

The rest of the article is organized as follows. In Sec. II we define the model and we analyze the bulk, surface, and line contributions to the free energy at zero temperature $T=0$. We derive the relationships among thermodynamic fields at the wetting transition for both surface and line terms. In Sec. III we present results for this model at $T>0$, within the mean-field approximation, and obtain the corresponding phase diagrams. In Sec. IV we summarize our results and give an outlook on future developments.

II. THE MODEL

A spin-$\frac{1}{2}$ Ising model on a cubic lattice with an edge formed by two nonparallel surfaces gives rise to line inhomogeneities of the type described in the Introduction for systems where there is simultaneous equilibrium of four phases. Two of these phases can be taken to be inert and their interfaces with the rest of the system are represented by two perpendicular (planar) surfaces or walls Γ_1 and Γ_2. The other two phases correspond, e.g., to two oppositely magnetized domains when the temperature T is below the Curie temperature T_c. The model is then characterized by the Hamiltonian (with spins $s_i = \pm 1$)

$$H(\{s\}) = -J \sum_{\{ij\}} s_i s_j - J_1 \sum_{\{ij\}\in\Gamma_1} s_i s_j - J_2 \sum_{\{ij\}\in\Gamma_2} s_i s_j - J_e \sum_{\{ij\}\in\Gamma_e} s_i s_j - H_1 \sum_{i\in\Gamma_1} s_i - H_2 \sum_{i\in\Gamma_2} s_i - H_e \sum_{i\in\Gamma_e} s_i \, , \quad (1)$$

where J is the bulk nearest-neighbor coupling; J_1 and J_2 the surface nearest-neighbor couplings on surfaces Γ_1 and Γ_2, respectively; J_e the nearest-neighbor coupling at the edge Γ_e where the two surfaces Γ_1 and Γ_2 meet, and H_1 the surface field acting at the "active" wall Γ_1. We take the surface field H_2 for Γ_2 to be always zero. That is, Γ_2 is a "neutral" wall and makes a 90° contact angle with the Ising model interface, in a semi-infinite geometry where Γ_1 is absent. Finally, H_e is an *edge field* acting on Γ_e. The spin lattice is shown in Fig. 2(a).

The total free energy of the system

$$F = fV + \sigma_1 A_1 + \sigma_2 A_2 + \tau L \quad (2)$$

contains bulk (fV), surface ($\sigma_1 A_1 + \sigma_2 A_2$), and line ($\tau L$) contributions. Here f is the bulk free-energy density on a volume V, σ_i the surface tension acting on surface Γ_i with area A_i ($i=1,2$), and τ is the total line tension associated with the line inhomogeneities (at the edge, or elsewhere) of length L.

Consider the active surface Γ_1 with surface field $H_1 > 0$. The magnet is at bulk two-phase coexistence and

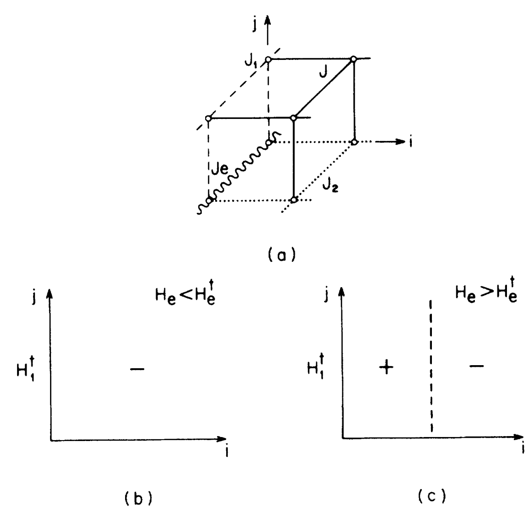

FIG. 2. (a) The spin lattice for a quadrant with two surfaces with different surface (dotted and dashed lines) and edge bonds (wiggly lines). This geometry is used to study the wetting transition at a contact line. In (b) the disfavored state (−) is close to the active wall. In (c) the preferentially adsorbed state (+) is close to the wall and a domain wall separates this state from the (−) state at the far right end of the figure.

we denote the phases by (+) and (−). In this case Γ_1 preferentially adsorbs the (+) phase. The surface free energy $\sigma_1=\sigma_{1+}$, generated when the (+) phase is chosen in bulk, is smaller than the surface free energy $\sigma_1=\sigma_{1-}$ of the disfavored state with the (−) phase in bulk. In the latter case there are two possible configurations for the magnetization profile: The partial wetting configuration with a nearly uniform phase extending down to Γ_1 and the complete wetting configuration where the (+) phase intrudes between Γ_1 and the bulk (−) phase [see Figs. 2(b) and 2(c)]. Clearly, the latter configuration includes a (+−) interface, infinitely far from Γ_1, with surface tension $\sigma_0=\sigma_{+-}$. Suppose now that we impose the disfavored state and vary one or more of the thermodynamic fields, so that a wetting phase transition takes place at Γ_1, from a state with $\sigma_{1-}<\sigma_{1+}+\sigma_{+-}$ to a state with $\sigma_{1-}=\sigma_{1+}+\sigma_{+-}$. Since the local external field acting on spins on the surface Γ_2 is zero, the surface tensions of the (+) and the (−) phases against this wall are the same, i.e., $\sigma_2=\sigma_{2+}=\sigma_{2-}$, so that the neutral wall is indifferent to this transition.

For the Hamiltonian (1), the wetting transition at Γ_1 [the transition from Fig. 2(b) to Fig. 2(c)] is obtained when the wetting condition

$$\sigma_{1-}=\sigma_{1+}+\sigma_{+-} \tag{3}$$

is first reached, because in the thermodynamic limit, surface contributions to the total free energy overwhelm line terms. The novel phenomenon we want to discuss is most clearly appreciated using an analogy with the ordinary wetting transition just described. Clearly, when the wetting transition is considered, it is assumed that the system is *at* two-phase coexistence in *bulk*. Similarly, the contact-line transition we propose is one that assumes the two-phase coexistence of the *surface* states of partial and complete wetting. That is, we will move *along* the first-order wetting phase boundary. In general, other interesting contact-line phenomena may occur when the wetting phase boundary is traversed, but we are not concerned with those here. (Analogously, interfacial phenomena other than the wetting transition are possible when crossing the *bulk* phase boundary.)

At the first-order wetting transition, we consider the line tensions τ_-^e, τ_+^e, and τ_0. The first two of these denote the excess free energies due to the inhomogeneities generated at the Γ_e edge when the (−) and the (+) phases are, respectively, in contact with Γ_1. The line tension τ_0 arises where the (+−) interface meets the wall Γ_2. Now, a "wetting" transition for the contact line occurs when the line tensions first satisfy Antonov's rule assuming one initially has $\tau_-^e<\tau_+^e+\tau_0$, i.e.,

$$\tau_-^e=\tau_+^e+\tau_0 \ . \tag{4}$$

Clearly, this transition can be brought about by changing, e.g., H_e.

Zero-temperature analysis

The total energy of the spin system can be easily determined at zero temperature, since then the magnetization at site i is $m_i=\pm 1$. The energy E^- of the system, when all spins are aligned in the (−) state, is

$$\begin{aligned}E^-=-3JV&+[J/2-2(J_1-J)+H_1]A_1\\&+[J/2-2(J_2-J)]A_2\\&+[-2J+3(J_1+J_2)/2-J_e+H_e-H_1]L \ ,\end{aligned} \tag{5}$$

and the energy E^+ of the system with all of its spins in the (+) state is

$$E^+=E^- -2H_1A_1-2H_eL+2H_1L \ , \tag{6}$$

while that for the (+−) interface is

$$E^0=2JA_1+2(J_2-J)L \ . \tag{7}$$

At the wetting transition (for the surface) $H_1=J$, since then the surface contributions to E^- and E^++E^0 are the same. In the present geometry, the wetting transition for the contact line takes place when the line terms first satisfy Antonov's rule, Eq. (4), for the line tensions, which corresponds to $H_e=H_1+(J_2-J)$. Since the wetting condition ($H_1=J$) also holds, this reduces to $H_e=J_2$.

III. MEAN-FIELD APPROXIMATION FOR FINITE TEMPERATURE

For $T>0$ we adopt the lattice mean-field theory which is known to give a first-order wetting phase boundary [12]. The model is translationally invariant with respect to the direction along the Γ_e edge, and its total mean-field free energy per unit length (along that direction) can be written as

$$\begin{aligned}F=\frac{kT}{2}&\left[\sum_{i=0}^{N}\sum_{j=0}^{N}(1+m_{i,j})\ln(1+m_{i,j})+\sum_{i=0}^{N}\sum_{j=0}^{N}(1-m_{i,j})\ln(1-m_{i,j})\right]\\&-J\sum_{i=0}^{N}\sum_{j=0}^{N}m_{i,j}(m_{i,j+1}+m_{i+1,j}+m_{i,j})-(J_1-J)\sum_{j=0}^{N}m_{0,j}(m_{0,j+1}+m_{0,j})\\&-(J_2-J)\sum_{i=0}^{N}m_{i,0}(m_{i+1,0}+m_{i,0})-(J_e+J-J_1-J_2)m_{0,0}^2-H_1\sum_{j=1}^{N}m_{0,j}-H_em_{0,0} \ ,\end{aligned} \tag{8}$$

where i and j are the column and row indexes, respectively, for a site in the lattice, $i=0$ defines the Γ_1 plane; $j=0$ the Γ_2 plane, and $i=j=0$ the Γ_e edge. The equilibrium magnetization profile $m_{i,j}$ satisfies the Euler-Lagrange equation

$$kT\ln\frac{(1+m_{i,j})}{(1-m_{i,j})}-2J(2m_{i,j}+m_{i+1,j}+m_{i-1,j}+m_{i,j+1}+m_{i,j-1})=0\ , \tag{9}$$

with boundary conditions

$$Jm_{-1,j}=H_1+(J-J_1)(m_{0,j+1}+m_{0,j-1}+2m_{0,j})\ , \tag{10a}$$

$$Jm_{i,-1}=(J-J_2)(m_{i+1,0}+m_{i-1,0}+2m_{i,0})\ , \tag{10b}$$

and

$$J(m_{-1,0}+m_{0,-1})=2(J_e-J)m_{0,0}+(J_1-J)m_{0,1}+(J_2-J)m_{1,0}\ . \tag{10c}$$

Furthermore, the equilibrium solution is that which minimizes F. The equations are solved numerically by simple iteration methods in a 100×100 lattice with additional boundary conditions $m_{i+1,j}=m_{i,j}$, $m_{i,j+1}=m_{i,j}$ at the free edges of the lattice. The wetting transition is determined first via the solution of Eq. (9) in the limit of large j (far away from the neutral wall Γ_2). In this limit, the boundary conditions (10b) and (10c) are irrelevant and the relevant fields are kT/J, J_1/J, and H_1/J. For fixed J_1/J we locate the regions where there are two solutions in (kT,H_1) space (in units of J). One corresponds to a partial wetting state where the magnetization is negative (the disfavored state for $H_1>0$). The other corresponds to a wetting state where the magnetization is positive (the favored state) near Γ_1, and is negative for large i, far away from Γ_1.

The discreteness of the model introduces a series of layering phase transitions describing the layer-by-layer growth of the wetting film [12]. These transitions shift to low temperature as the value of the surface interaction J_1 increases. Since we are interested here in the description of the first-order wetting transition, we restricted our numerical calculations to values of $J_1\geq1.5\ J$, for which these layering transitions are absent within a temperature interval $[T_c/2,T_c]$. In Figs. 3(a) and 3(b) we show the wetting phase diagram for both surface and line transitions. In these figures points under and above the dashed curves correspond, respectively, to partial and complete wetting states. The solid curves on these figures give the values of the edge field $H_e=H_e^t$ at which the wetting transition for the contact line takes place. The value of H_e^t for each temperature is determined under the wetting condition $H_1=H_1^t$. In Fig. 4 we show a plot of the total free energy for both partial and complete wetting states of the contact line [Figs. 2(b) and 2(c)] at constant temperature, as we vary the edge field H_e.

For values of the wall coupling J_2 with $0<J_2<aJ$, with $a>1$, the contact-line transition field H_e^t decreases with temperature and vanishes at the bulk critical temperature T_c. As shown in Fig. 3(a) for $J_2=J$, H_e^t may pass through zero at some $T<T_c$. As we increase the value of J_2 a *pure edge transition* can take place at $T>T_c$. This is possible when there is a *pure surface transition* at Γ_2. As is well known [7,8], this happens for surface couplings J_2 larger than a critical surface coupling aJ that in this cubic lattice and in mean-field theory takes the value $a=\frac{5}{4}$. When $J_2/J>\frac{5}{4}$, spins on Γ_2 can order at temperatures above the bulk Curie temperature, in which case the system behaves as a two-dimensional system. A typical phase diagram for this case is depicted in Fig. 3(b).

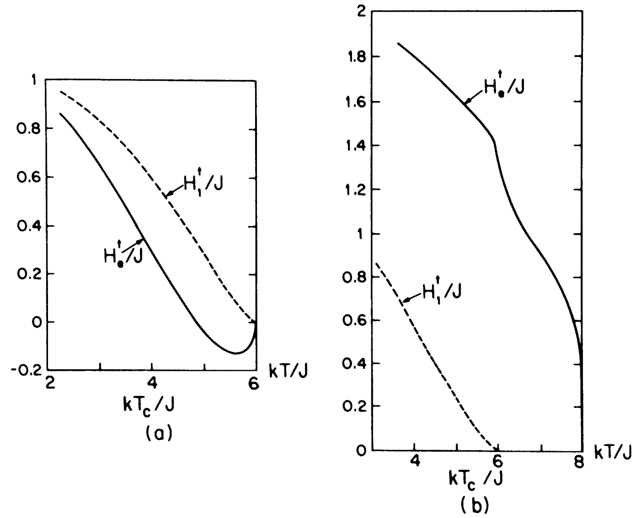

FIG. 3. Phase diagrams for the ordinary wetting transition $H_1=H_1^t$ and contact-line wetting transition $H_e=H_e^t$ (both in units of the bulk coupling J) when $J_1=1.5$ J. In (a) $J_2=J$ and in (b) $J_2=2J$.

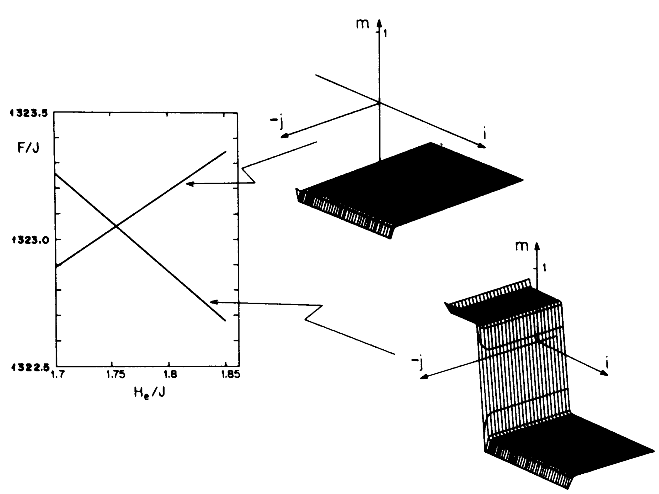

FIG. 4. Total free energy F for the 100×100 lattice for different values of the edge field H_e. The two curves show the values of F for the two possible states whose magnetization profiles in the (i,j) plane are shown in the insets and which correspond to the configurations in Figs. 2(b) and 2(c).

IV. SUMMARY AND DISCUSSION

We have studied a model where an Ising magnet is bounded by two planar surfaces which meet at an edge. This geometry was considered in a number of earlier works on wetting and layering phenomena [13]. The phase transition for the contact line has not, to our knowledge, been addressed previously, although Gibbs has already discussed the basic thermodynamics involved [11]. As relevant fields we have considered, in addition to the surface couplings J_1 and J_2 and a wall field H_1, an edge coupling J_e and an edge field H_e. Both the zero-temperature and the mean-field solution of the model indicate that one may find a wetting transition for the contact line, occurring under the overall surface-field conditions for the usual wetting transition, as the edge parameters are varied. The condition that the line tensions must satisfy *at* and *beyond* the wetting transition for the contact line corresponds to the rule of Antonov (familiar in the context of interfacial tensions) applied to the three line tensions involved.

When the neutral wall permits surface ordering above the bulk critical temperature, the contact-line wetting transition is very similar to the known (critical) wetting transition of a truly two-dimensional system [14]. Our mean-field solutions in general indicate a first-order wetting transition for the contact line. The fluctuations that we ignored are expected to be important in these low-dimensional structures. As is seen in the example of the two-dimensional wetting transition, to which our problem reduces in the limit $J \rightarrow 0$ (with J_2 remaining constant), the fluctuations will, in general, not destroy the contact-line wetting transition but rather affect its order (first order $\rightarrow$ continuous). On the other hand, fluctuations are likely to destroy the would-be prewetting transition extensions of the contact-line transitions.

The thermodynamic properties of three-phase lines are not easily accessible experimentally. They are delicate and overwhelmed by surface and bulk effects. The phenomenon that we have described here might turn out to be conspicuous and observable in macroscopic systems, and become a suitable experimental, or computer simulation, test ground to study the properties of line inhomogeneities in three-dimensional systems. Very recently, we learned that J. W. Cahn [15] examined the dissociation of a four-phase contact line among Teflon (substrate), a methanol-rich liquid, a cyclohexane-rich liquid, and air, into two three-phase contact lines as a function of the concentration of water that is dissolved into the liquid phases. This is qualitatively similar to the transition from Fig. 1(b) to Fig. 1(c), with the modification that in Cahn's setup one liquid phase is inside the other.

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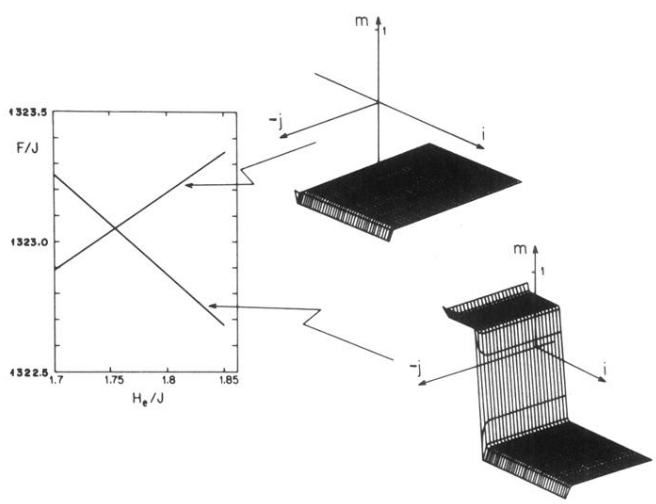

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