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Does the Interface Experience the van der Waals Loop?

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A discussion is given of the role of the unstable and metastable parts (the "loop") in the equation of state of the van der Waals or Landau type for the interface theory. The role of the loop in the field-theoretic renormalization calculation of the interface is analyzed. It is shown that in real-space renormalization no loop occurs and that a satisfactory interface calculation can be made using Migdal's renormalization procedure.

KEY WORDS: Equation of state; metastability; interface; capillary waves; renormalization.

INTRODUCTION

In the late 1950s, when Eddie Cohen was a driving force behind the activities at the Institute for Theoretical Physics in Amsterdam, the theory of phase transitions was at an impasse. On one hand, there was a substantial effort at developing improved approximations of the Kikuchi type for lattice models(1) and at deriving integral equations for the correlation functions of a liquid such as the hypernetted chain equation.(2) These theories did predict phase transitions, but very much in the way of the equation of state derived by van der Waals(3) in 1873. On the other hand, also rigorous theorems(4) were then emerging, showing that instabilities in the equation of state (the "loop" in the van der Waals equation) do not occur in a proper evaluation of the partition function.

The approximate theories yield a liquid and a vapor branch. The phase transition must be located by finding two phases of equal temperature, pressure, and thermodynamic potential just as Maxwell's equal-area construction does for the van der Waals loop. In the approximate

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theories there is no distinction between the physical parts outside and the unphysical parts inside the coexistence region.

Thus, at that time the somewhat depressing conclusion was that nothing but an exact evaluation of the partition function could produce a proper phase transition.

The loop in the van der Waals equation gives a continuous transition from the liquid to the vapor state. Already in 1871 (2 years before the thesis of van der Waals!) Thompson(5) speculated about such a continuous connection, suggesting that in the interface region between a coexisting liquid and vapor, states of matter were realized with densities between the liquid and vapor densities, which do not exist as homogeneous bulk phases.

There is a stubborn folklore that the continuation of the stable branches represents the metastable branches of the equation of state. This suggestion is tempting because an experimenter often realizes the metastable branches quite simply without noticing in the data that the coexistence point has been passed.[2] If one accepts, however, that equilibrium statistical mechanics boils down to a decent evaluation of the partition function (which only gives the stable branches), then one has to be optimistic to believe that an error in the calculation explains a non-equilibrium problem such as metastability. One may speculate that the exact equation of state can be continued analytically into the coexistence region. However, neither the possibility of continuation is likely(7) nor the relation to metastability clear.(8)

Yet it is not so simple to dismiss the loop as an artefact of a simple-minded approximation. Presumably its greatest stronghold is the role in the theory of the interfacial profile, which again started with van der Waals.(9) As it is the reference point for this paper, I start out with a brief summary of its structure.

1. THE CLASSICAL INTERFACE THEORY

In Landau's version, phrased in the magnetic language, the classical interface theory supposes the existence of a free energy density $f(m)$ as a function of the magnetization m (or order parameter) and a free energy functional of the form

$$\mathscr{F}[m] = \int d\mathbf{r} \left\{ f(m(\mathbf{r})) + \frac{A}{2} |\nabla m(\mathbf{r})|^2 \right\} \tag{1.1}$$

The function $f(m)$ has the form of a double-well potential for temperatures below the critical temperature. The second term represents the effect on the

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[2] Among the wealth of evidence some striking examples can be found in ref. 6.

free energy due to inhomogeneities. In a planar geometry an interface profile depends only on one coordinate z and obeys the boundary conditions

$$m(z) = \pm m_{\text{sp}}, \qquad z \to \pm\infty \tag{1.2}$$

where m_{sp} is the spontaneous magnetization or bulk value of the order parameter. The profile that satisfies (1.2) and minimizes $\mathscr{F}[m]$ satisfies the equation

$$A \frac{d^2m}{dz^2} = \frac{\partial f}{\partial m} = h(m) \tag{1.3}$$

In a homogeneous phase $h(m)$ would be the magnetic field associated with the magnetization m. Figure 1 sketches a profile and the function $h(m)$, from which one sees the necessity of a loop in $h(m)$. The profile equation (1.3) has the form of Newton's equation of motion, with A playing the role of a mass, the order parameter m as position, coordinate z as time, and $h(m)$ as force or $-f$ as potential. The motion occurs between the minima of $f(m)$. Starting at $z = -\infty$ with a negative m, it has to be "accelerated" by a positive field $h(m)$ and for $z > 0$, where m becomes positive, it has to be "deaccelerated" by a negative field. So field and magnetization have to be opposite in the interface region, which means a loop in the magnetic equation of state $h(m)$. Thus, the interface experiences the loop and nothing else of the equation of state, as was anticipated by Thompson.

Several arguments can be raised against this theory.(10) The squared gradient in (1.1) is too simple to represent the free energy contributions due to inhomogeneities. At best, it suffices near the critical point, where the interface is thick and spatial variations in $m(z)$ are slow. For lower tem-

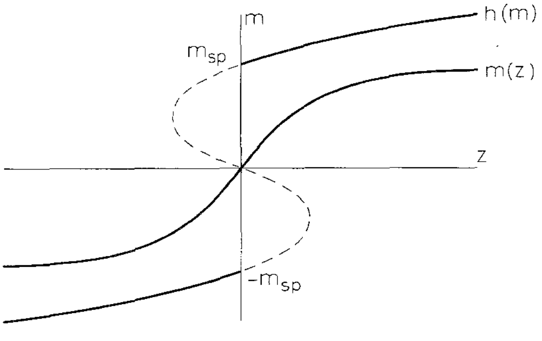

Fig. 1. Magnetization profile $m(z)$ and associated magnetic field $h(m)$ in the classical equation (1.3) for the interface. The loop in the equation of state is indicated by the dashed part. Note that profile and field are opposite for the same magnetization value.

peratures where steep gradients in the interface must be expected, the squared gradient must be replaced by a more detailed molecular expression involving the direct correlation function.(11)

Near the critical point, (1.3) fails to incorporate properly the critical fluctuations in the same way as the standard mean field theory fails for bulk critical phenomena. The critical exponent for the surface tension as following from (1.3) obeys the scaling laws for mean field exponents. Fisk and Widom(12) have repaired this shortcoming by proposing a shape for the loop which is consistent with the critical scaling behavior. Thus, scaling properties for the interface could be derived in full agreement with bulk critical behavior.

Interpolations for the equation of state or the correlation functions from the bulk branches into the coexistence region have, however, no firm foundation and consequently demonstrate a certain arbitrariness. Fortunately, the shape of the resulting interface is rather insensitive to the precise interpolation expression, but this reflects more the general plainness of interface profiles than a justification for the interpolation procedure.

The most severe objection against the classical interface theory as embodied by (1.3) (or sophistication thereof) is that it leads to an intrinsic interface. In Fig. 1 I have taken the symmetry point $m=0$ at $z=0$, which is arbitrary. The location of the interface has to be found from such boundary conditions as the total mass of the liquid–vapor system or the net magnetization in the spin system. But apart from this global constraint, the classical interface theory does not need an external agent to give the interface its shape. Buff *et al.*,(13) showed, however, that in low dimensions $d \leqslant 3$ the interface is unstable against surface or capillary waves.

To see their point, let us denote the transverse coordinate (along the interface) by $\mathbf{r}_\perp$ and the local deviation of the interface from its equilibrium position by $h(\mathbf{r}_\perp)$. Then, for sufficiently smooth $h(\mathbf{r}_\perp)$, the energy of a deviation is given by

$$E[h] = \int d\mathbf{r}_\perp \, \{\sigma[1 + |\nabla h(\mathbf{r}_\perp)|^2]^{1/2} + \tfrac{1}{2} g \, \Delta\rho \, h^2(\mathbf{r}_\perp)\} \tag{1.4}$$

The first term accounts for the increase in area due to the displacement $h(\mathbf{r}_\perp)$. So σ is the surface tension of the interface. The second term is added in view of its future importance. It represents the gravitational energy of a column $h(\mathbf{r}_\perp)\, d\mathbf{r}_\perp$ of height $h(\mathbf{r}_\perp)$. Thus, $\Delta\rho$ is the mass density difference between the phases.

For smooth $h(\mathbf{r}_\perp)$ the gradients are small and one may expand the square root and introduce Fourier components such that

$$E[h] = \frac{1}{2} \int \frac{d\mathbf{k}_\perp}{(2\pi)^{d-1}} \, (\sigma k_\perp^2 + g \, \Delta\rho) \, |h_{\mathbf{k}_\perp}|^2 \tag{1.5}$$

where $h_{\mathbf{k}_\perp}$ are the Fourier components of $h(\mathbf{r}_\perp)$. If one then assumes that these waves are thermally excited with a Boltzmann weight, the partition function for the capillary waves is Gaussian, enabling us to calculate all desired properties. The mean square displacement of the waves is found as

$$\langle h^2 \rangle = \int \frac{d\mathbf{k}_\perp}{(2\pi)^{d-1}} \frac{k_B T}{\sigma k_\perp^2 + g\,\Delta\rho} \tag{1.6}$$

Now the importance of the gravitational term is clear. The sum over $\mathbf{k}_\perp$ is a $(d-1)$-dimensional integral and for $d \leqslant 3$ the expression (1.4) diverges for $g = 0$ at the low-$\mathbf{k}_\perp$ side. For small $\mathbf{k}_\perp$ the expression (1.5) can be trusted, as these waves lead to very smooth $h(\mathbf{r}_\perp)$. For small g, (1.6) behaves as

$$\begin{aligned} \langle h^2 \rangle &\sim g^{(d-3)/2}, \qquad && d < 3 \\ &\sim |\ln g| && d = 3 \end{aligned} \tag{1.7}$$

Taking this result seriously, one must conclude that $\langle h^2 \rangle$ rather than the intrinsic width following from (1.3) sets the scale for the interface width. Thus, we must expect the interface to behave for $g \to 0$ as

$$\begin{aligned} m(z; g) &= m(zg^{(3-d)/4}), \qquad && d < 3 \\ &= m(z/|\ln g|^{1/2}) && d = 3 \end{aligned} \tag{1.8}$$

This forces us to think differently about the profile. Not only its location, but also its shape is severely affected by the external conditions. Without a gravity-type field the size of the system will provide a cutoff in the divergent expression (1.5). I will limit the considerations in this paper to an external field such as gravity for the liquid–vapor transition or a linearly varying magnetic field for the magnetic systems.

The capillary wave theory is neither consistent nor complete. One could argue$^{(14)}$ that the fluctuations of the interface are fluctuations in the microscopic configurations which are already taken into account in the free energy expression (1.1). One can hold also that, if the capillary waves are a real contribution, then they must also contribute to the surface tension. Thus, σ occurring in (2.3) must be some bare surface tension to be completed by the capillary waves to the full or experimentally observed surface tension.

Apart from the σ, the capillary wave theory needs also a large-$k_\perp$ cutoff as input. This cutoff is necessary to make (1.5) convergent at the large-$k_\perp$ side for $d = 3$. Clearly, it does not make sense to speak about a capillary wave of a wavelength comparable to the interparticle distance.

Even the thickness of the intrinsic profile, which supposedly displays the waves, should be considered as a lower-wavelength limit. The choice of the cutoff is more delicate then is usually assumed.(15) I will come back to this point in the next section.

Capillary waves are a real phenomenon. Direct evidence has been obtained by molecular dynamics simulations of two-dimensional systems.(16) Indirect evidence follows from optical reflectivity measurements(17) and X-ray scattering(18) on liquid–vapor interfaces.

The logical step to integrate the classical interface theory and the capillary wave theory is to see (1.1) as the proper starting point having (1.3) as the optimal profile, of which the fluctuations still have to be taken into account. Likely the capillary wave fluctuations are dominant. This of course is the viewpoint of the renormalization approach, which I summarize in the next section.

2. THE INTERFACE IN RENORMALIZATION FIELD THEORY

The renormalization approach starts with a subtle difference in interpretation of the right-hand side of (1.1). Rather than a free energy, it is seen as a Hamiltonian for the order parameter field $m(\mathbf{r})$

$$\mathscr{H}[m] = \int d\mathbf{r} \left\{ f(m(\mathbf{r})) + \frac{A}{2} |\nabla m(\mathbf{r})|^2 \right\} \tag{2.1}$$

For this change in interpretation a new meaning has to be given to $f(m)$ and A. Let $m(\mathbf{r})$ be a smooth distribution of the magnetization, e.g., with only Fourier components of wavenumber $k < k_c$, where k_c is small with respect to microscopic wavenumbers and large with respect to macroscopically realizable wavenumbers. Then consider $m(\mathbf{r})$ as a given constraint and calculate the free energy due to all configurations generated by fluctuations of $m(\mathbf{r})$ with wavenumber $k > k_c$. The idea is that this free energy can be represented by the integrand of (2.1), i.e., that a function $f(m)$ and a constant A can be found. The so-defined function $f(m)$ may display a double-well structure at low temperatures. This is not against any rigorous theorem, since $f(m)$ is not directly related to the bulk free energy. The latter is obtained from (2.1) by integrating over all $m(\mathbf{r})$ with Fourier components $k < k_c$:

$$e^{-\beta F} = \prod \int dm(\mathbf{r})\, e^{-\beta \mathscr{H}[m]} \tag{2.2}$$

For a specific system it must be considered a hopeless task to calculate an actual $f(m)$ or A, since the constraint of given $m(\mathbf{r})$ makes the problem more difficult than a direct calculation of the bulk free energy. The $f(m)$ and A will also depend on the choice of k_c. The renormalization theory calculates how $f(m)$ and A change under a change of k_c or, what is equivalent, under a change in scale. Near the critical point a number of quantities are found to be insensitive to the details of $f(m)$. For these universal properties the precise form of $f(m)$ is irrelevant. Thus the difficult task of determining $f(m)$ can be avoided and at the same time the universal properties apply to a wide class of systems. Of course, the results are limited to the critical region, which can be loosely defined as the region dominated by the long-wavelength fluctuations of $m(\mathbf{r})$.

The universal quantities can only be extracted systematically in an expansion in the parameter $\varepsilon = 4 - d$. Ohta and Kawasaki(19) started the renormalization program for the interface by calculating the profile to first order in ε. They found that the scaling properties for the interface proposed by Widom(20) are satisfied. Setting $\varepsilon = 1$ or $d = 3$, their interface is numerically close to the Fisk–Widom profile. One has to be cautious in seeing this as a justification for the Fisk–Widom theory. To order ε, they managed to write the profile equation in the form (1.3), thus providing a function $h(m)$ in the coexistence region. Comparing this function with the Fisk–Widom interpolation, they notice differences, but one can qualify these as minor. More important is that their trick to derive an equation of the form (1.3) works only to order ε and relies heavily on the explicit mean-field form for $m(z)$ in zeroth order in ε. In reality, the profile equation does not have the simple form (1.3), but is a nonlinear integral equation for $m(z)$. So the fluctuations change $h(m)$ into a nonlocal relation.

An interesting side remark is that Ohta and Kawasaki compare their $h(m)$ with the analytical continuation of $h(m)$ from outside the coexistence region into the coexistence region. Again to order ε, such an extrapolation exists and it *diverges* at the spinodal of the zeroth-order mean-field expression. Apart from the fact that one does not know what such divergence means, one has the problem that the continuation must be made *before* the powers in ε are exponentiated, which has to be done in order to obtain the correct critical exponents. After the exponentiation the critical singularities forbid an analytical continuation. Therefore one cannot say that the ε expansion supports the classical equation (1.3).

The ε expansion misses the difficulties associated with the capillary waves, which start to become divergent for $d = 3$ or $\varepsilon = 1$. The influence of capillary waves in the renormalization theory has been studied by Jasnow and Rudnick.(21) As no systematic expansion exists in $d = 3$, their results are based on the one-loop approximation. They find that the interface width diverges as $|\ln g|^{1/2}$ and that $m(z)$ has a shape as indicated in (1.7). The approximation cannot be considered as accurate enough to allow a detailed comparison with experimentally measured interface profiles.(17) When quantities like the correlation length are used as adjustable parameters a reasonable fit is obtained.

A more phenomenological approach has been taken by Sengers and van Leeuwen.(22) Following Weeks,(23) they argued that critical fluctuations up to a certain wavelength do lead to an intrinsic interface which can be described by the Fisk–Widom theory. The longer-wavelength fluctuations are dominantly given by the capillary wave theory. Thus, the Fisk–Widom surface tension is the bare value entering the capillary wave Hamiltonian. The other constants of the capillary wave theory are fixed as follows. There is a well-known discrepancy between the Fisk–Widom critical amplitude for the surface tension and the measured value.(24) This is attributed to the capillary wave contribution to the surface tension. Usually one does not pay much attention to the renormalization of the surface tension due to the capillary waves since the effect is finite. As was noted by Kayser,(15) it requires another parameter in Week's column model(23) to make the capillary wave picture precise. This parameter is used by Sengers and van Leeuwen to fit the capillary wave contribution to the measured value.

Once the idea is accepted that the capillary waves contribute to the surface tension, one is more or less forced to the notion of a wavelength-dependent surface tension. The measured value is the long-wavelength limit and the bare value some short-wavelength value. Small wavelengths contribute to the surface tension felt by the longer waves. In the capillary wave theory such a renormalization is absent because the waves are independent modes. Nevertheless it is easy to incorporate the idea in a self-consistent way.(22) In this line of thought the short-wavelength cutoff is fixed by the condition of minimal renormalization. Thus, a capillary wave theory is constructed without adjustable parameters for the interface profile. The agreement with the so-determined profiles and the experimental data of Wu and Webb(17) is good, but typical gravity or cutoff effects are not borne out by the experiments. Whether this is a real discrepancy or a pushing of relatively old experiments beyond their limits can only be settled by more accurate data. Such new experiments might then also reveal information on the narrow transition zone near T_c where the interface below T_c smoothly goes over in a field-induced order parameter profile above T_c.(27)

In conclusion, one may say that renormalization has the loop as input on some bare level, which is then made diffuse (nonlocal) by the fluctuations. Such a diffuse loop cannot qualify as an extension of the equation of state into the coexistence region and its sole application is in the theory of the interface profile.

For a full discussion of the interface profile near and far below the critical point a more ambitious renormalization program starting from the microscopic Hamiltonian is needed. This program exists for lattice systems, albeit less well founded and systematic than the field-theoretic approach. It is called real-space renormalization and the remainder of this paper is intended to show how interfaces come about in this theory.

3. THE INTERFACE IN REAL-SPACE RENORMALIZATION

Let us consider an Ising model on a d-dimensional lattice with a varying magnetic field H_i in the Hamiltonian

$$\mathscr{H}[s] = \sum_i H_i s_i + K \sum_{\langle ij \rangle} s_i s_j \tag{3.1}$$

K is the coupling constant between a neighboring pair $\langle ij \rangle$. The field H_i has the form

$$H_i = g z_i \tag{3.2}$$

where z_i is the z coordinate of site i. The field gradient g plays the role of the gravity constant for a fluid. The interface will settle around the plane $z = 0$.

A real-space renormalization transformation is a map of $\mathscr{H}[s]$ onto a new $\mathscr{H}'[s']$, where the new spins $s'_{i'}$ are located on a new lattice of which the lattice distance is b times the old lattice distance. In general $\mathscr{H}'[s']$ will not be of the same simple structure as (3.1). It will contain usually all kinds of coupling constants, but for meaningful transformations $\mathscr{H}'[s']$ must be dominantly governed by a field $H'_{i'}$ and nearest-neighbor coupling constants $K'_{i'}$. We include all constants under a general label $K_{\alpha i}$, where α is the type of interaction and i its location. In (3.1) the nearest-neighbor coupling constant is the same for all neighbor pairs, but we must be prepared that the spatial inhomogeneity due to H_i transfers in the renormalization process to all coupling constants.

We represent the renormalization transformation by the set of equations

$$\begin{aligned} H'_{i'} &= H'_{i'}[H_i, K_{\beta i}] \\ K'_{\alpha i'} &= K'_{\alpha i'}[H_i, K_{\beta i}] \end{aligned} \tag{3.3}$$

In principle, $H'_{i'}$ depends on all the fields H_i and coupling constants $K_{\beta i}$, but we require that the transformation is approximately local, i.e., $H'_{i'}$ is mainly determined by the H_i and $K_{\beta i}$ in the neighborhood of site i'. We have to formulate the equations in their general form, as they have to be applied repeatedly and the special character (3.1) is lost soon.

The free energy of the system characterized by H_i, $K_{\alpha i}$ is a functional $F[H_i, K_{\alpha i}]$ and transforms under (1.3) to

$$F[H_i, K_{\alpha i}] = G[H_i, K_{\alpha i}] + F[H'_{i'}, K'_{\alpha i'}] \tag{3.4}$$

where $G[H_i, K_{\alpha i}]$ is the spin-independent constant which is formed under renormalization.

The magnetization can be defined as

$$m_i = \delta F[H_i, K_{\alpha i}]/\delta H_i \tag{3.5}$$

and thus variation of (3.4) with respect to H_i yields

$$m_i = \delta G/\delta H_i + \sum_{i'} \left\{ m'_{i'}(\delta H'_{i'}/\delta H_i) + \sum_{\beta} e'_{\beta i'}(\delta K'_{\beta i'}/\delta H_i) \right\} \tag{3.6}$$

where $e_{\alpha i}$ is the abbreviation of

$$e_{\alpha i} = \delta F/\delta K_{\alpha i} \tag{3.7}$$

We see from (3.6) that the various derivatives of the free energy couple and thus (3.6) has to be supplemented by an equation for $e_{\alpha i}$ which follows from variation of (3.4) with respect to $K_{\alpha i}$,

$$e_{\alpha i} = \delta G/\delta K_{\alpha i} + \sum_{i'} \left\{ m'_{i'}(\delta H'_{i'}/\delta K_{\alpha i}) + \sum_{\beta} e'_{\beta i'}(\delta K'_{\beta i'}/\delta K_{\alpha i}) \right\} \tag{3.8}$$

The derivatives in (3.6) and (3.8) follow from the renormalization equations (3.3) and the expression for $G[H_i, K_{\alpha i}]$. So Eqs. (3.6) and (3.8) relate the set $\{m_i, e_{\alpha i}\}$ to the set $\{m'_{i'}, e'_{\alpha i'}\}$ of the renormalized system.

Repeated renormalization generally drives the system to an extreme situation: very weakly coupled systems (high temperatures) or very strongly coupled systems (low temperatures). In the extreme situations, $\{m_i, e_{\alpha i}\}$ must be determined directly from the Hamiltonian. We will refer to these values as boundary conditions on the renormalization flow. In order to find m_i for the original system (3.1), we must apply the renormalization process twice. First we carry out the transformation (3.3), with (3.1) as input, sufficiently many times such that an extreme situation has evolved in which we know how to calculate $\{m_i, e_{\alpha i}\}$. Then we retrieve our steps in (3.3) and calculate simultaneously from (3.6) and (3.8) the set $\{m_i, e_{\alpha i}\}$ in the previous system until the starting Hamiltonian has been reached and the corresponding $\{m_i, e_{\alpha i}\}$ are found.

This process is the same as the one by which the equation of state of a homogeneous bulk system can be determined. Then we have spatially independent $H_i = H$ and $K_{\alpha i} = K_\alpha$. The transformation (3.3) simplifies to

$$\begin{aligned} H' &= H'(H, K_\beta) \\ K'_\alpha &= K'_\alpha(H, K_\beta) \end{aligned} \tag{3.9}$$

For the homogeneous version of (3.6) and (3.8) we must take into account that the number of sites N in the old system is b^d times the number of new sites:

$$\begin{aligned} m &= N^{-1}(\partial G/\partial H) + b^{-d}\left[m'(\partial H'/\partial H) + \sum_\beta e'_\beta(\partial K'_\beta/\partial H)\right] \\ e_\alpha &= N^{-1}(\partial G/\partial K_\alpha) + b^{-d}\left[m'(\partial H'/\partial K_\alpha) + \sum_\beta e'_\beta(\partial K'_\beta/\partial K_\alpha)\right] \end{aligned} \tag{3.10}$$

The function $m(H, K)$ follows by renormalizing the (H, K) system to an extreme situation where m and e_α can be calculated. Then, going back to the original system, repeated application of (3.10) yields the desired $m(H, K)$.

Before embarking on the discussion of the solution of the inhomogeneous case, I indicate the behavior of $m(H, K)$. Figure 2 is a sketch of the flow lines of the renormalization process. On the basis of this picture, one may distinguish three regimes, as follows.

a) The High-Temperature Regime. Here $K < K_c$, where K_c is the critical coupling. Repeated renormalization will drive the coupling to zero and the system becomes a free system. There the magnetization is given by

$$m = \tanh H_f \tag{3.11}$$

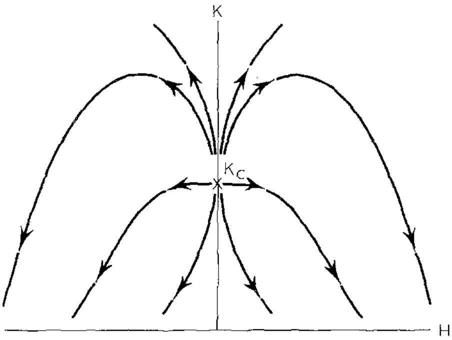

Fig. 2. Flow lines of the renormalization for Migdal's scheme (4.1). Here $K = K_c$, $H = 0$ is the unstable (critical) fixed point. The line $K = 0$ is a line of stable fixed points.

where H_f is the field which has been developed from the original field. Similar expressions can be given for the e_α. From this boundary condition the curves $m(H, K)$ can be obtained.

b) The Low-Temperature Regime. Now $K > K_c$ and repeated renormalization leads to strong coupling. At the same time any finite $H > 0$ will grow to large values, while $H < 0$ will decrease to large, negative values. The boundary condition is therefore

$$m = \pm 1 \qquad H \gtrless 0 \tag{3.12}$$

and similar expressions for the e_α, because a strongly coupled system in an external field is fully magnetized. The sudden jump in the boundary condition when H passes through $H = 0$ is responsible for the spontaneous magnetization in the original system. It is interesting to note that this renormalization only produces stable branches of the equation of state even when the procedure is approximate. By symmetry, magnetization and field are always of the same sign.

c) The Critical Regime. Here $K \cong K_c$ and it takes the renormalization process a long time to produce couplings outside the critical regime either $K > K_c$ or $K < K_c$. In the mean time the field grows rapidly. By the time the trajectory leaves the critical region, the field is usually sizable (when the initial H is not too small) and it continues to grow further. So it does not make much difference whether the boundary condition (3.11) or (3.12) is applied. On the way back the magnetization is broken down along the flow line, which takes longer the closer one started out near the critical point $K = K_c$, $H = 0$. So the spontaneous magnetization disappears at criticality and the equation of state joins continuously from above and below K_c.

For the inhomogeneous system (3.1) one may consider the local approximation

$$m_i^{\text{loc}} = m(H_i, K) \tag{3.13}$$

which follows by ignoring all nonlocalities in (3.6) and (3.8). In the high-temperature regime this is a smooth curve for small gradients g, which justifies the approximation. Near K_c and small z the local approximation develops strong gradients which develop into a jump below K_c. Then the local approximation fails and nonlocal aspects in (3.6) and (3.8) will smooth out the local curve to a continuous interface.

To be more precise, an actual realization of the renormalization is needed. In the next section I describe the results of a simple but illuminating approximation due to Migdal.(25)

4. MIGDAL'S APPROXIMATION

Figure 3 shows a $b \times b$ section of a $(d=2)$-dimensional (square) lattice. The idea is to change the scale by eliminating the spins which are not on the corners. In order to do this, couplings inside the square are moved to the edges as indicated by the arrows. With only bonds along the edges, the intermediate spin on the edges can be eliminated by a one-dimensional decimation which induces a coupling between the corner spins and a new field on the corner sites. Considering the corners as the sites of the new system, a new Hamiltonian for the corner spins results which again has a field term and a nearest-neighbor interaction. For our purpose it is very attractive that Migdal's scheme can be implemented in arbitrary dimension d and for arbitrary rescaling factor b. We use the latter to study the generator of the transformation by taking $b=1+dt$, where dt is an infinitesimal increase in scale. Without derivation I present here the main formulas; the details are given elsewhere.(26)

The homogeneous renormalization equation can be written as

$$\begin{aligned} \partial H/\partial t &= 2d\dot{H}(H, K) \\ \partial K/\partial t &= (d-1)\,K + \dot{K}(H, K) \end{aligned} \tag{4.1}$$

where $\dot{H}$, $\dot{K}$, and the spin-independent constant $\dot{g}$ (taking the role of G/N) are given by

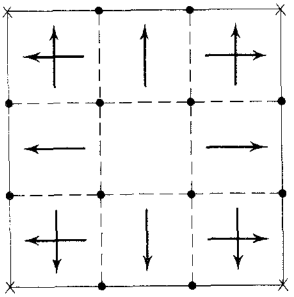

Fig. 3. A $b \times b$ section $(b=3)$ of a square lattice. The dashed internal bonds are moved to the edges as indicated by the arrows, enforcing the edge bonds by a factor b^{d-1}. No magnetic fields are moved. The corners are the sites of the renormalized lattice.

$$\begin{aligned}\dot{H}(H, K) &= -(\tanh H)\, \dot{K}(H, K)\\ \dot{K}(H, K) &= -\frac{1-e^{-4K}}{4q(H, K)} \ln \frac{1+q(H, K)}{1-q(H, K)}\\ \dot{g}(H, K) &= K + \tfrac{1}{2} \ln(1-e^{-4K}) - (c \tanh 2K)\, \dot{K}(H, K)\end{aligned} \tag{4.2}$$

with the auxiliary function

$$q(H, K) = [\tanh^2 H + e^{-4K}(1-\tanh^2 H)]^{1/2} \tag{4.3}$$

Equations (4.1) give the rate of change of H and K with an increment in scale. The corresponding flow equation for the magnetization m and the nearest-neighbor correlation e take the form

$$\begin{aligned}\partial m/\partial t &= d(m - \dot{T}_H)\\ \partial e/\partial t &= e - \dot{T}_K\end{aligned} \tag{4.4}$$

where T_x is the x derivative $(x = H, K)$ of the linear expression in m and e

$$\dot{T}_x = \frac{\partial \dot{g}}{\partial x} + 2m \frac{\partial \dot{H}}{\partial x} + e \frac{\partial \dot{K}}{\partial x} \tag{4.5}$$

So one sees that the three functions $\dot{H}$, $\dot{K}$, and $\dot{g}$ fully determine the flow of the Hamiltonian (4.1) and the flow of the magnetization (4.4). The bulk relation $m(H, K)$ can be found from (4.1) and (4.4) as indicated in the previous section.

The next step is the flow equations for the inhomogeneous case. Here we have a different situation for the Hamiltonian parameters H and K and the derivatives of the free energy m and e. Playing with the initial gradient g, one can make the spatial variation of the Hamiltonian arbitrarily small. During the renormalization process the gradients will grow, but they are still controlled by the input value of g. So nonlocal effects in the Hamiltonian flow can be made small by letting $g \to 0$. The inhomogeneous equivalent of (4.1) becomes

$$\begin{aligned}\partial H(z, t)/\partial t &= z\, \partial H(z, t)/\partial z + 2d\dot{H}(H(z, t), K(z, t))\\ \partial K(z, t)/\partial t &= z\, \partial K(z, t)/\partial z + (d-1)\, K(z, t) + \dot{K}(H(z, t), K(z, t))\end{aligned} \tag{4.6}$$

The terms with $z(\partial/\partial z)$ arise from the renumbering of the sites in the scaling process.

In contrast, the nonlocal aspect cannot be ignored in the flow for m and e. The reason is that arbitrarily small g can still lead to large gradients in the magnetization, as the local approximation (3.13) shows. The flow equations for $m(z, t)$ and $e(z, t)$ may be written in first approximation$^{(26)}$ as

$$\begin{aligned}\frac{\partial m(z,t)}{\partial t}&=z\frac{\partial m(z,t)}{\partial z}+d[m(z,t)-\dot{T}_H]+\left(\frac{\partial m}{\partial t}\right)_{\rm nl}\\ \frac{\partial e(z,t)}{\partial t}&=z\frac{\partial e(z,t)}{\partial z}+[e(z,t)-\dot{T}_K]\end{aligned}\tag{4.7}$$

$\dot{T}_H$ and $\dot{T}_K$ are the same expression (4.5) now involving $H(z, t)$, $K(z, t)$, $m(z, t)$, and $e(z, t)$. The nonlocal contribution to the magnetization flow is given by

$$\left(\frac{\partial m}{\partial t}\right)_{\rm nl}=\left(\frac{1}{12}-\frac{1}{2}\frac{\partial \dot{H}}{\partial H}\right)\frac{\partial^2 m(z,t)}{\partial z^2}\tag{4.8}$$

In principle, all higher derivatives and combinations thereof occur, but (4.8) gives the dominant term, provided that $m(z, t)$ is still a relatively smooth function of z.

One can make Eqs. (4.6) and (4.7) somewhat more transparant by removing the spatial rescaling term through the transformation

$$H(z,t)=\hat{H}(ze^{t-t_f},t)\tag{4.9}$$

Here t_f is the duration of the renormalization, which I discuss later. Inserting (4.9) and similar expressions for the other fields into (4.6) and (4.7), one finds the flow of the Hamiltonian

$$\begin{aligned}\frac{\partial \hat{H}}{\partial t}&=2d\dot{H}(\hat{H},\hat{K})\\ \frac{\partial \hat{K}}{\partial t}&=(d-1)\hat{K}+\dot{K}(\hat{H},\hat{K})\end{aligned}\tag{4.10}$$

and for the magnetization

$$\begin{aligned}\frac{\partial \hat{m}}{\partial t}&=d[\hat{m}-\dot{T}_H]+e^{2(t-t_f)}\left(\frac{1}{12}-\frac{1}{2}\frac{\partial \dot{H}}{\partial H}\right)\frac{\partial^2 \hat{m}(v,t)}{\partial v^2}\\ \frac{\partial \hat{e}}{\partial t}&=[\hat{e}-\dot{T}_K]\end{aligned}\tag{4.11}$$

To avoid confusion, I have indicated the spatial argument of $\hat{m}(v, t)$ by $v=z\exp(t-t_f)$. One sees that v does not occur explicitly in (4.10), but only as an argument of $\hat{H}$ and $\hat{K}$. So the solution of (4.10) is for each v a local problem as a consequence of the fact that we have ignored nonlocal aspects in the Hamiltonian flow. In (4.11) v occurs explicitly as a second derivative in the nonlocal flow term. For the solution of (4.10) and (4.11) we must start with the initial values

$$\begin{aligned} \hat{H}(v, 0) &= H(ve^{t_f}, 0) = ge^{t_f}v \\ \hat{K}(v, 0) &= K(ve^{t_f}, 0) = K \end{aligned} \tag{4.12}$$

calculate the final fields $\hat{H}(v, t_f) = H(v, t_f)$ etc., impose the boundary conditions

$$\hat{m}(v, t_f) = m(v, t_f), \qquad \hat{e}(v, t_f) = e(v, t_f) \tag{4.13}$$

role back the solution (4.10), and compute the change in the magnetization through (4.11), with the result

$$m(v, 0) = \hat{m}(ve^{-t_f}, 0) \tag{4.14}$$

Qualitatively it is easy to see what the nonlocal term does to the profile. At the start of the backflow it acts as a diffusion term. Its influence dies out quickly through the exponential factor in front of it. I discuss the three regimes mentioned in the previous section.

In the high-temperature regime the boundary condition (3.11)

$$\hat{m}(v, t_f) = \tanh \hat{H}(v, t_f) \tag{4.15}$$

is a smooth function, as $\hat{H}(v, t_f)$ is weakly dependent on v for small g. Not surprisingly, the influence of the nonlocal terms is vanishing and the local approximation gives the profile.

In the critical regime two growth rates play a role. For $H \to 0$ and $\tau = K - K_c \to 0$ the flow (4.1) reduces to

$$\begin{aligned} \partial H/\partial t &\simeq y_H H \qquad \text{or} \qquad H(t) \simeq e^{y_H t} H \\ \partial \tau/\partial t &\simeq y_T \tau \qquad \text{or} \qquad \tau(t) \simeq e^{y_T t} \tau \end{aligned} \tag{4.16}$$

These formulas apply as long as H and τ are small. The magnetization m varies in the critical regime as [see (4.4)]

$$\partial m/\partial t \simeq (d - y_H)\, m \qquad \text{or} \qquad m(t) \simeq e^{(d - y_H)t} m \tag{4.17}$$

The trajectory leaves the critical regime when $\tau(t)$ is of order unity. We take this as a measure for the duration t_f,

$$e^{-y_T t_f} = |\tau| \tag{4.18}$$

The field gradient grows in t_f to

$$g_f = e^{(y_H+1)t_f} g = g\,|\tau|^{-(y_H+1)/y_T} \tag{4.19}$$

The parameter g_f will be a characteristic of the behavior of $\hat{m}(v, t_f)$. With (4.14) and (4.17) we find

$$m(v, 0) = |\tau|^{(d-y_H)/y_T}\,\hat{m}(v\,|\tau|^{1/y_T}, 0) \tag{4.20}$$

If we could forget the dependence of $\hat{m}$ on g_f for a moment, we would have Widom's scaling law$^{(10)}$ for the interface. The power in front of $\hat{m}$ gives the magnitude of the spontaneous magnetization below T_c and the power inside gives the correlation length ξ, since

$$\xi = \xi_0\,|\tau|^{-1/y_T} \tag{4.21}$$

The dependence of $\hat{m}$ on g_f is, however, important. To see the behavior for $\tau \to 0$ we exchange τ for g and write in place of (4.20)

$$m(z; g, \tau) = g^{(d-y_H)/(y_H+1)}\,\tilde{m}(z g^{1/(y_H+1)}, \tau g^{-y_T/(y_H+1)}) \tag{4.22}$$

a scaling form which has been proposed earlier.$^{(27)}$ In (4.22) one can set $\tau = 0$ and the critical dependence of the profile on z and g follows.

The scaling property (4.22) is a general feature of the critical interface profile. The precise shape of $\tilde{m}$ must follow from the boundary condition. For $K = K_c$ (or $\tau = 0$) there is a problem in the center of the system $z \simeq 0$, since the center coupling $K(0, t) = K_c$ remains critical. Thus, one cannot use the free system boundary condition (4.15) nor the low-temperature condition $m = 1$. The best compromise is to impose the local value at a time t_f when most of the system has moved away from criticality.$^{(26)}$

In the low-temperature regime a similar problem arises with the local boundary condition

$$\hat{m}(v, t_f) = \operatorname{sign} v \tag{4.23}$$

which varies too fast at $v = 0$ to allow the expression (4.8) to be valid. In the large-K regime the flow equations simplify to

$$\begin{aligned} &\partial\hat{H}/\partial t d\hat{H} &&\text{or}\quad \hat{H}(t) = e^{dt}\hat{H} \\ &\partial\hat{K}/\partial t = (d-1)\,\hat{K} &&\text{or}\quad \hat{K}(t) = e^{(d-1)t}\hat{K} \end{aligned} \tag{4.24}$$

while the flow of the magnetization is controlled by the nonlocal term

$$\partial\hat{m}(v, t)/\partial t = (1/6)\,e^{2(t-t_f)}\,\partial^2\hat{m}(v, t)/\partial v^2 \tag{4.25}$$

This diffusion equation can be solved explicitly,

$$\hat{m}(v, t) = \int_{-\infty}^{\infty} dv' \frac{e^{-(v-v')^2/D(t)}}{[\pi D(t)]^{1/2}} \hat{m}(v', t_f) \tag{4.26}$$

with

$$D(t) = \tfrac{2}{3} \int_t^{t_f} e^{2(t'-t_f)}\, dt' \tag{4.27}$$

The picture is that after a finite initial period the trajectory reaches the large-K regime where (4.26) applies. For large t_f we may translate the solution in terms of the gradient g, which grows as

$$g(t) = e^{(d+1)t} g \tag{4.28}$$

So

$$e^{-t_f} = (g/g_f)^{1/(d+1)} \tag{4.29}$$

The magnetization at $t=0$ is then, according to (4.14),

$$m(v, 0) = \hat{m}(v(g/g_f)^{1/(d+1)}, 0) \tag{4.30}$$

with $\hat{m}(v, 0)$ given by (4.26) and $D(0) \simeq 1/3$ (for t_f large). For large t_f the system develops a steeper and steeper gradient and one expects that $\hat{m}(v, t_f)$ approaches the step function (4.23). This gives a definite limit to $\hat{m}(v, 0)$ and to $m(v, 0)$ except for the value of g_f. As mentioned, the validity of (4.25) breaks down for too steep gradients and so the t_f and g_f must be chosen with care. Information can be obtained from the $d=1$ case, where Migdal's procedure is exact [but (4.25) still approximate]. Taking $g_f=3$ and $\hat{m}(v, t_f)$ given by (4.23), the exact $d=1$ profile follows.(28) Thus, $g_f=3$ and (4.23) is a good combination in any dimension.(26)

From (4.30) one sees a behavior which resembles the capillary wave result. The dimensional dependence is, however, different. If we expand around $d=1$

$$\begin{aligned} \frac{1}{d+1} &\simeq \frac{1}{2} - \frac{d-1}{4} + \cdots \\ \frac{3-d}{4} &\simeq \frac{1}{2} - \frac{d-1}{4} \end{aligned} \tag{4.31}$$

we see that the powers agree near $d=1$, where Migdal gives the correct trend.(25)

5. DISCUSSION

The classical theory of interfaces relates the interfacial profile to hypothetical homogeneous phases with densities in the coexistence region. These hypothetical phases result from some extension of the stable branches into the coexistence region (the "loop"). Fur such extension no foundation can be found in equilibrium statistical mechanics, neither in homogeneous bulk systems nor in coexisting phases separated by an interface region.

A loop may occur at some mesoscopic or bare level using the order parameter as main variable to describe the configurations of the system. At this level the classical theory describes the interface, but the fluctuations change the interfacial theory drastically to a nonlocal relation between order parameter and conjugated field.

Renormalization on a microscopic level does not lead to a loop in any stage. Only the stable branches are obtained, not only on a rigorous level, but also approximately. Consequently, this renormalization theory for the interface does not involve any unstable or metastable parts of the equation of state. In the renormalization process the interface probes thermodynamic phases further away from coexistence rather than hypothetical phases in the coexistence region.

The results described in this paper are based on renormalization of an Ising spin system on a lattice. Due to universality, the critical behavior of the interface should be the same as that for fluid interfaces. Whether the results can be extended to fluid interfaces further away from the critical point depends on the question of whether renormalization of the fluid on a microscopic level is possible. Conceptually there seems no problem, but the results are so far not very reliable.(29)

The interfaces discussed here display the correct scaling behavior in the critical regime. Improved renormalization procedures will lead to improved scaling functions. The situation is different in the low-temperature regime, where a scaling behavior is found which differs in exponent from the behavior expected from the capillary wave theory. Both exponents are determined on dimensional grounds. Thus, a simple improvement in renormalization technique will not yield a better exponent. Rather, the structure of the flow at low temperatures has to be improved. In fact, one could argue that it is sufficient to impose a different boundary condition, which reflects properly the capillary waves as they occur, e.g., in the solid-on-solid model. Once the correct capillary wave behavior is in the boundary condition, it propagates to the whole low-temperature regime. So the problem is really to find a renormalization procedure which treats correctly the waves in a solid-on-solid model in its low-temperature phase.

Migdal's procedure is too one-dimensional to describe properly the capillary waves. To find the necessary improvements for low temperatures is the main goal for future research.

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