Journal of Statistical Physics, Vol. 37, Nos. 3/4, 1984

Field-Induced Phase Separation in One Dimension

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Received March 27, 1984; revision received June 11, 1984

Phase separation is induced in the one-dimensional Ising chain (or lattice-gas model of a fluid) by means of an external field that changes sign in the middle of the chain. The magnetization profile (or density profile of the analogous fluid) is obtained analytically. It is found to decay exponentially rapidly to the bulk-phase magnetizations (or densities), the exponential decay parameter being the correlation length in the bulk phases in the presence of the field. This is in accord with earlier theoretical ideas. The interfacial tension is also obtained analytically. In an appropriately defined limit of large neighboring-site spin–spin interactions and small external field the interface becomes infinitely broad while the amplitude of the profile and the interfacial tension both vanish, in close imitation of the approach to a critical point in a real fluid. In this asymptotic limit the interfacial tension is related to the amplitude of the profile in the way that is predicted by earlier theories of interfaces near critical points, with critical-point exponents now those appropriate to one dimension. The exact interfacial profile and tension are used to test several approximations, including a corrected form of the "barometric law" and local (square-gradient) and nonlocal forms of the van der Waals theory.

KEY WORDS: Ising chain; phase separation; interface; magnetization or density profile; surface tension.

1. MODEL INTERFACE

We present an exactly soluble one-dimensional model of an interface between coexisting phases, and with it we test some earlier hypotheses and approximations in the theory of interfaces in three dimensions. Our aim is thus the same as that of one of us[(1a)] and of Abraham and one of us[(1b)] who used exact methods to analyze the interface of the *d*-dimensional spherical model in the presence of an external field identical to the one we shall use in our

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model. Also related to our work is that of Clayton and Woodbury,(2) who studied field-induced interfaces in an Ising strip (although they then let the width of the strip increase, to make the model two-dimensional, whereas ours is always one-dimensional); that of Compagner,(3) who studied a one-dimensional system of attracting hard rods in the presence of gravity; of Percus,(4a) Robledo,(4b) and Robledo and Varea,(4c) who treated the hard-rod system in the presence of an arbitrary external field; of van Leeuwen and Hilhorst,(5) who analyzed the solid-on-solid model in two dimensions in the presence of various external fields; of Ebner *et al.*,(6) who treated a one-dimensional Lennard-Jones system both numerically and by approximate methods; and of Kinzel,(7) who studied the interface between phases in a one-dimensional Potts model (but with nonmacroscopic "phases" induced by boundary conditions rather than by an external field).

Our model is the one-dimensional Ising chain with nearest-neighbor interactions (or the equivalent lattice gas). We index the sites of the chain with a position coordinate z, and we associate with the site at z a spin variable $s_z = \pm 1$. Neighboring spins, at sites z and $z+1$, interact with energy $-Js_z s_{z+1}$ with $J > 0$, so the interaction favors parallel spin alignment. There is no spontaneous phase separation in such a one-dimensional system, but we induce it with an external field $\mathscr{H}(z)$ that changes sign in the middle of the chain (Fig. 1a):

$$\mathscr{H}(z) = \begin{cases} H, & z > 0 \\ 0, & z = 0 \\ -H, & z < 0 \end{cases} \tag{1.1}$$

with $H > 0$. The energy of interaction between the spin and field at z is $\mathscr{H}(z)\, s_z$, so H, like J, has the dimensions of an energy.

Had there been no spin–spin interaction ($J = 0$), the resulting magnetization profile $m(z)$,

$$m(z) = \langle s_z \rangle \tag{1.2}$$

would have had the same z dependence as the external field $\mathscr{H}(z)$, as pictured in Fig. 1a; but because there is an interaction that favors parallel alignment ($J > 0$), the step is smoothed and the resulting profile $m(z)$ is as in Fig. 1b. (The density profile of the corresponding lattice gas is $\frac{1}{2}[1 + m(z)]$.) By symmetry,

$$m(-z) = -m(z) \tag{1.3}$$

For convenience we imagine $\mathscr{H}(z)$ and $m(z)$ to be functions of a continuous variable z, and we picture them that way in Fig. 1, although they are defined only for integer z.

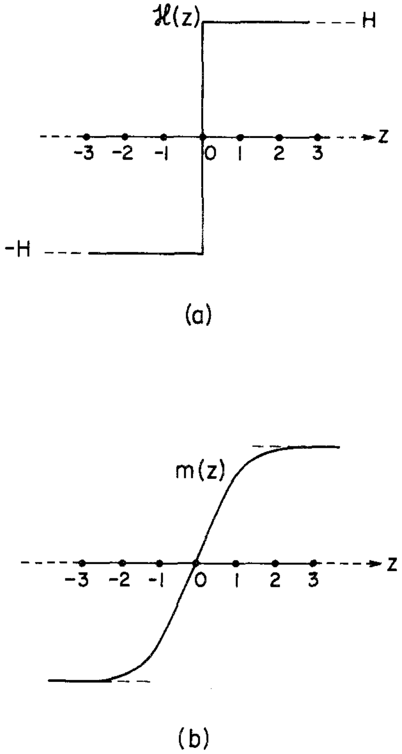

Fig. 1. (a) Field $\mathscr{H}(z) = H$ (for $z > 0$), 0 (at $z = 0$), $-H$ (for $z < 0$), (b) Magnetization profile $m(z)$.

At large $|z|$, where $m(z)$ is close to its asymptotic limits, we have the two coexisting bulk phases, each one uniform. Between them, at small $|z|$, is the interface, which is the object of our study. As we expect and shall see, the bulk phase at $z > 0$ is the same (in particular, its magnetization $m(\infty)$ is the same) as that in a model with the same J but with a uniform field H at all z; while the phase at $z < 0$ is the same (in particular, its magnetization $m(-\infty)$ is the same) as in a model with the same J but with a uniform field $-H$ at all z. Thus, each phase influences the other only over a finite distance definable as the thickness of the interface. This thickness is microscopic; again as we expect and shall see, it is essentially the correlation length in a model with the same J but with a uniform field H at all z. The interfacial thickness is finite because the field, in addition to creating the interface, also pins it in place and thus keeps it from wandering and smearing out the profile $m(z)$.

In Section 2 we display the model's magnetization profile $m(z)$, and in Section 3 the interfacial tension. The latter, which in this one-dimensional system has the dimensions of an energy, is the difference between the free energy of the model system pictured in Fig. 1 and that of a reference system which is the same as the model system except that the field has the uniform value H (or, equivalently, $-H$) at all z. We separate the interfacial free energy of the present model into an extrinsic part and an intrinsic part, of which the former is the integrated direct interaction of the spins in the profile $m(z)$ with the external field, while the latter is their integrated direct interaction with each other. Both parts of the interfacial tension depend on both J and H because the profile $m(z)$ does. It is the intrinsic part that is to be compared with the surface tension in models in which phase separation is spontaneous.

In Section 4 we observe that the limit $J/kT \to \infty$ and $(H/kT)\exp(2J/kT) \to 0$ (with k Boltzmann's constant and T the absolute temperature) imitates the approach to a critical point, for in that limit the bulk magnetizations $m(\infty)$ and $m(-\infty)[=-m(\infty)]$, the reciprocal ξ^{-1} of the interfacial thickness ξ, and σ/kT, where σ is the interfacial tension, all vanish. Further, we find that σ/kT, ξ, and $m(\infty)$ are then asymptotically related in just the way scaling theories have suggested they are related in real interfaces, although here the critical-point exponents are those appropriate to one dimension. In this limit, also, the extrinsic part of σ becomes negligible compared with the intrinsic part, so the separation of σ into its two components is inconsequential.

Since the magnetization (or density) profile and interfacial tension in this model are known explicitly and exactly, we are able to use them to test some approximations that are like ones commonly applied in the theory of interfaces. These include a corrected form of the "barometric law" and various local (square-gradient) and nonlocal mean-field theories. The approximate and exact profiles are compared in Section 5, and the approximate and exact surface tensions in Section 6. Our results are discussed briefly in Section 7.

2. MAGNETIZATION (DENSITY) PROFILE

The model is just a one-dimensional Ising model with nearest-neighbor interactions, so even with the external field (1.1) the profile $m(z)(=\langle s_z\rangle)$ may be found by elementary transfer-matrix methods. One finds that

$$m(z) = m(\infty)(1 - e^{-z/\xi}), \qquad z \geqslant 0 \tag{2.1}$$

with

$$e^{-1/\xi} = \frac{\cosh(H/kT) - [\sinh^2(H/kT) + e^{-4J/kT}]^{1/2}}{\cosh(H/kT) + [\sinh^2(H/kT) + e^{-4J/kT}]^{1/2}} \tag{2.2}$$

and

$$m(\infty) = \{1 + [e^{2J/kT} \sinh(H/kT)]^{-2}\}^{-1/2} \tag{2.3}$$

$m(z)$ for $z < 0$ is obtained from (2.1) by (1.3).

The profile (2.1) with (1.3) is qualitatively of the form anticipated in Fig. 1b. Thought of as a function of a continuous variable z it has a discontinuous second derivative at $z = 0$. This is an artificiality of the model, but it is too mild a singularity to be readily visible. We refer to it again in Section 5.

The ξ and $m(\infty)$ given by (2.2) and (2.3) are precisely the correlation length (i.e., the exponential decay parameter of the spin–spin correlation function) in units of the lattice spacing,(8a) and the magnitude of the uniform magnetization per spin,(8b) respectively, for the Ising chain in a uniform field of magnitude H. Thus, although in the present model the phase separation is not spontaneous but is induced by the external field (1.1), the profile $m(z)$ nevertheless has the form that, at least near the critical point, it is found to have in theories of the type of the van der Waals theory(9); viz.,

$$m(z) = m^* f(z/\xi) \tag{2.4}$$

where m^* is the spontaneous magnetization, ξ the correlation length in the bulk phases, and f a universal odd function of argument z/ξ, with $f(\infty) = 1$. That the profile in our model is of the form (2.4) for all values of H/kT and J/kT, and not only as the critical point is approached, is an accident of the model's simplicity and not otherwise significant.

3. SURFACE TENSION

The free energy of the model pictured in Fig. 1 is greater than that of a reference system of the same number of sites, with the same spin–spin interactions, but with a uniform field H at every site. The free energy of this one-phase reference system is an even function of H, and, per site, is the same as that of either of the two limiting bulk phases in the model two-phase system. Therefore, in the thermodynamic limit—i.e., in the limit in which the number of sites in the model and in the reference system, while remaining equal, both become infinite, while the interface in the former remains in the middle—the difference between the free energies of the two systems is just that of the interface. It is the one-dimensional analog of a surface tension in three dimensions or of a boundary tension in two dimensions, although here it has the dimensions of an energy rather than of an energy per unit area or length. Nevertheless, because of the analogy with three dimensions we call it the "surface tension" of our one-dimensional model, and symbolize it by σ. We may then evaluate it as

$$\sigma/kT = -\lim \ln(Z/Z_0) \tag{3.1}$$

where Z and Z_0 are the partition functions of the model two-phase system and of the reference one-phase system, respectively, while "lim" means the thermodynamic limit described above.

The evaluation of Z and Z_0 for this one-dimensional system is again elementary by conventional transfer-matrix methods. We find at the thermodynamic limit

$$\sigma/kT = \tfrac{1}{2} \ln[1 + e^{4J/kT} \sinh^2(H/kT)] \tag{3.2}$$

By (2.3), this may also be expressed in terms of the bulk magnetization $m(\infty)$,

$$\sigma/kT = \tfrac{1}{2} \ln\{1 + [m(\infty)^{-2} - 1]^{-1}\} \tag{3.3}$$

These formulas for σ, like that for the profile in Section 2, are exact for the model two-phase system.

We may call the derivative

$$E = \left(\frac{\partial \sigma/kT}{\partial 1/kT}\right)_{J,H} \tag{3.4}$$

the surface energy, and decompose it into two parts E_e and E_i,

$$E = E_e + E_i \tag{3.5}$$

given, respectively, by

$$E_e = H \left(\frac{\partial \sigma/kT}{\partial H/kT}\right)_{J/kT} = H \frac{\sinh(H/kT)\cosh(H/kT)}{e^{-4J/kT} + \sinh^2(H/kT)} \tag{3.6}$$

and

$$\begin{aligned} E_i = J \left(\frac{\partial \sigma/kT}{\partial J/kT}\right)_{H/kT} &= 2J\{1 + [e^{2J/kT} \sinh(H/kT)]^{-2}\}^{-1} \\ &= 2Jm(\infty)^2 \end{aligned} \tag{3.7}$$

The extrinsic surface energy E_e is the difference, between the two-phase model and the one-phase reference system, of the energies of interaction of the spins with the respective external fields in the two systems; while the intrinsic surface energy E_i is the corresponding difference, between the two systems, of the energies of interaction of the spins with each other.

An important check of consistency is to note that E_e may be directly evaluated from the profile $m(z)$:

$$E_e = -\sum_{z=-\infty}^{\infty} [\mathscr{H}(z)\, m(z) - Hm(\infty)] \tag{3.8}$$

with $\mathscr{H}(z)$ as in (1.1). From (3.8) with (1.3) and (2.1)–(2.3) we again obtain (3.6).

Corresponding to (3.5) we may define a decomposition of σ into extrinsic and intrinsic parts,

$$\sigma = \sigma_e + \sigma_i \tag{3.9}$$

related to E_e and E_i, respectively, by the analogs of (3.4),

$$\left(\frac{\partial \sigma_e/kT}{\partial 1/kT}\right)_{J,H} = E_e, \qquad \left(\frac{\partial \sigma_i/kT}{\partial 1/kT}\right)_{J,H} = E_i \tag{3.10}$$

Although there is no arbitrariness in the decomposition of E into E_e and E_i by (3.4)–(3.7), the decomposition of σ into σ_e and σ_i by (3.9) and (3.10) is arbitrary to within a constant multiple of kT, which may be added to one of these two components while it is subtracted from the other. With one choice of this arbitrary element we obtain from (3.6), (3.7), and (3.10),

$$\sigma_e/kT = H \int_0^{1/kT} \frac{\sinh(Hx)\cosh(Hx)}{e^{-4Jx} + \sinh^2(Hx)}\, dx \tag{3.11}$$

$$\sigma_i/kT = 2J \int_0^{1/kT} \{1 + [e^{2Jx}\sinh(Hx)]^{-2}\}^{-1}\, dx \tag{3.12}$$

and we may now add an arbitrary constant (or function of J and H, but independent of T) to this σ_i/kT provided we also subtract it from this σ_e/kT. But such an additional constant, if it were anything other than 0, would make either σ_i or σ_e negative at high temperature, where the right-hand sides of (3.11) and (3.12), as they now stand, become small.

The point of this decomposition of σ is to remove from it, as far as possible, any artificialities due to the field $\mathscr{H}(z)$, to make the resulting surface tension more properly comparable with that in systems in which phase separation is spontaneous. In the present model the field $\mathscr{H}(z)$ contributes to the surface energy E of (3.4) in two ways, one essential and one incidental. Its essential effect is to create the interface of profile $m(z)$ given by (2.1) and (1.3). Because of the inhomogeneity described by this profile there is an excess spin–spin interaction energy, over that in the uniform reference system, of amount E_i (>0) given by (3.7). This intrinsic surface energy still depends on H, but only because the profile does. There is an additional component of the surface energy, the extrinsic component E_e, also positive, which is the excess, over that in the uniform reference system, of the energy of interaction of the spins with the external field. This is the incidental effect of the field. Only that part of the surface energy that arises from the intrinsic structure of the interface, viz., E_i, is comparable with the surface energy in a system in which phase separation is spontaneous. We now wish to do the same for the surface tension: to remove from σ any incidental effect of the external field so as to identify that part which is due only to the structure of the interface. The two parts should both be proper free-energy excesses arising from the inhomogeneity, and therefore, in particular, should both be positive always. We saw that, as long as the decomposition is defined by (3.9) and (3.10), only the σ_e and σ_i of (3.11) and (3.12) satisfy this condition. We then take (3.12) to be the intrinsic interfacial free energy of the model.

In the next section we imitate approach to a critical point, at which the surface tension vanishes. We find that σ_e vanishes more rapidly than σ_i, so the former becomes a negligible part of the total σ and the decomposition of σ is then inconsequential.

4. APPROACH TO THE CRITICAL POINT

At the critical point of a phase equilibrium the correlation length ξ becomes infinite while the bulk-phase magnetization (or difference of the bulk-phase densities) vanishes. Thus, the interfacial thickness diverges at the same time that the amplitude of the profile vanishes, and the interface becomes infinitely diffuse.

In the present model, for ξ to diverge requires

$$J/kT \to \infty, \qquad H/kT \to 0 \tag{4.1}$$

by (2.2). For $m(\infty)$ to vanish at the same time requires, by (2.3), that H/kT vanish even more rapidly than $\exp(2J/kT)$ diverges, and so, more specifically than (4.1),

$$J/kT \to \infty, \qquad (H/kT)\exp(2J/kT) \to 0 \tag{4.2}$$

From the more restrictive conditions (4.2), which assure $m(\infty) \to 0$, we have from (3.3),

$$\sigma/kT \sim \tfrac{1}{2}m(\infty)^2 \tag{4.3}$$

so σ/kT also vanishes, as at a real critical point.

This is true also with the σ_i of (3.12) in place of the total σ. From (3.12),

$$\sigma_i/kT = (2J/kT) \int_0^1 \{1 + [e^{2Jy/kT} \sinh(Hy/kT)]^{-2}\}^{-1} \, dy \tag{4.4}$$

But H/kT vanishes faster than $\exp(2J/kT)$ diverges, according to (4.2), so H/kT vanishes faster than $\exp(2Jy/kT)$ diverges, for all $0 \leqslant y \leqslant 1$. Therefore, from (4.4), in the limit (4.2),

$$\begin{aligned} \sigma_i/kT &\sim (2J/kT)(H/kT)^2 \int_0^1 y^2 e^{4Jy/kT} \, dy \\ &\sim \tfrac{1}{2}(H/kT)^2 \, e^{4J/kT} \end{aligned} \tag{4.5}$$

so from (2.15), in the same limit

$$\sigma_i/kT \sim \tfrac{1}{2} m(\infty)^2 \tag{4.6}$$

This is the same as (4.3), as asserted. We conclude from (3.9), (4.3), and (4.6) that as the critical point is approached σ_e/kT vanishes even more rapidly than σ_i/kT does; that in this limit, therefore, σ_i becomes the whole of σ; and that the decomposition of σ into σ_e and σ_i is then inconsequential.

The relation (4.3) or (4.6) between the interfacial tension and the bulk-phase magnetization may be compared with the general scaling relation(9)

$$\sigma/kT \sim K(A/kT) \, m(\infty)^2/\xi \tag{4.7}$$

in which K is a positive constant of proportionality, and A/kT is related to the second moment of the direct correlation function $c(r)$ in the bulk phases by

$$A/kT = (1/2d) \int r^2 c(r) \, d\mathbf{r} \tag{4.8}$$

with d the dimensionality of the system. In (4.7) we have written $m(\infty)$ for $\rho_l - \rho_g$, the difference in density of the coexisting liquid and gas phases in the corresponding lattice gas, because $\rho_l = \tfrac{1}{2}[1 + m(\infty)]$ and $\rho_g = \tfrac{1}{2}[1 + m(-\infty)] = \tfrac{1}{2}[1 - m(\infty)]$. The argument of $c(r)$ is the distance from some arbitrarily chosen central molecule or between centers of a pair of molecules. In mean-field or Ornstein–Zernike approximation A/kT has a finite, positive limit as the critical point is approached, but more generally it diverges as

$$A/kT \sim \text{const}\ \xi^{\eta} \tag{4.9}$$

where "const" is a constant of proportionality, and where η is Fisher's exponent,$^{(10)}$ which is 0 in Ornstein–Zernike approximation or in systems of dimensionality $d \geqslant 4$, and approaches 1 as $d \to 1$.$^{(11)}$

For the present model, the Fourier transform $\tilde{c}(q)$ of the direct correlation function $c(r)$ is readily calculated in closed form, with the result (in lattice-gas language) that in the phase of density ρ

$$\tilde{c}(q) = -\frac{1}{1-\rho} + \frac{\cos q - \exp(-1/\xi)}{\rho(1-\rho)\sinh(1/\xi)}$$

Then from the discrete form of (4.8) in $d = 1$,

$$A/kT = \sum_{z=1}^{\infty} z^2 c(z) = -\tfrac{1}{2}\tilde{c}''(0)$$

we find

$$A/kT = [2\rho(1-\rho)\sinh(1/\xi)]^{-1}$$

As the critical point is approached [i.e., as $\rho \to 1/2$ and $\xi \to \infty$], we get

$$A/kT \sim 2\xi \tag{4.10}$$

Thus, we confirm (4.9) with $\eta = 1$, as found by Nelson and Fisher$^{(11)}$; and we see that, with this specifically one-dimensional value of the exponent η, our result (4.3) or (4.6) for the behavior of the surface tension on approach to the critical point is also in accord with the scaling relation (4.7). More specifically, from (4.3) [or (4.6)], (4.7), and (4.10), we have $K = \frac{1}{4}$. This value of the coefficient for $d = 1$ may be compared with the classical$^{(9)}$ $K = 1/6$, which holds for $d \geqslant 4$; with Binder's$^{(12)}$ estimate $K \simeq 0.092$ for $d = 3$; and with the $K \simeq 0.0428$ quoted by Binder$^{(12)}$ for $d = 2$. Our value for $d = 1$ is not a simple extrapolation of those for $d > 1$.

We expect also that as the critical point is approached the asymptotic proportionality$^{(9)}$

$$\sigma/kT \sim \xi^{-(d-1)} \tag{4.11}$$

will hold for dimensionality $d \leqslant 4$. This is equivalent to the exponent relation$^{(9)}$ $\mu = (d-1)\nu$, where ν and μ are the exponents that determine, respectively, the rate at which ξ diverges and that at which σ/kT vanishes. This would give $\mu = 0$ in our one-dimensional model (assuming ν to be finite); and so from (3.9), for the exponent β that determines the rate at which $m(\infty)$ vanishes, we would have $\beta = 0$, as found by Nelson and Fisher$^{(11)}$ for $d = 1$.

The vanishing of the exponents μ and β, which are associated, respectively, with σ/kT and $m(\infty)$, could mean either that the latter quantities do not vanish as the critical point is approached, or that they do vanish but more slowly than any positive power of $1/\xi$ (as $1/\ln \xi$, for example). Our model is consistent with either and we may choose either at will. If $m(\infty)$ is chosen to vanish, then so do σ/kT and σ_i/kT, by (4.3) and (4.6), while if $m(\infty)$ is chosen not to vanish, then (3.3) gives σ/kT also nonvanishing. We prefer to think of σ/kT and $m(\infty)$ as vanishing, i.e., to specify approach to the critical point by (4.2) rather than by the less restrictive (4.1), because the resulting physical picture is then more closely analogous to that in a real, three-dimensional system. Also, if $m(\infty)$ is not taken to vanish we do not have the simple scaling (4.3) or (4.6), which is the one-dimensional form of (4.7).

This exactly soluble model has proved to be fairly realistic in its description of the interfacial structure and tension, including their relation to each other and their behavior on approach to the critical point. The model should therefore be useful for testing approximations that are like those in common use in treating interfaces in three dimensions. That is the subject of Sections 5 and 6, in which we study approximations to the profile and to the tension, respectively.

5. APPROXIMATE PROFILE

5.1. Corrected "Barometric Law"

The simplest approximation to the magnetization profile $m(z)$ in a nonuniform field $\mathscr{H}(z)$ would be the analog of the "barometric law":

$$\mathscr{H}(z) \simeq I[m(z)] \tag{5.1}$$

where the function $I(m)$ is what would be the uniform field I were the system of uniform magnetization m. In the model we presented in Section 2, the external magnetic field is of the form $\mathscr{H}(z) = H \operatorname{sgn}(z)$ with $\mathscr{H}(0) = 0$, so the approximation (5.1) would yield the trivial result $m(z) = m(\infty) \operatorname{sgn}(z)$, $m(0) = 0$, with $m(\infty)$ the bulk magnetization given by (2.3). The interface would thus be infinitely sharp.

To obtain a nontrivial $m(z)$ we must correct (5.1), and we do so in a way suggested by the van der Waals theory of interfaces.$^{(9)}$ We thus take as the first of the approximations we shall test:

$$Am''(z) = I[m(z)] - \mathscr{H}(z) \tag{5.2}$$

where A is the constant given in (4.8) and is thus proportional to the second moment of the direct correlation function in either bulk phase, and where

$$I(m) = kT \operatorname{arcsinh} \frac{e^{-2J/kT} m}{(1-m^2)^{1/2}} \tag{5.3}$$

from (2.3) and the definition of $I(m)$.

Because the assumptions underlying the van der Waals theory of interfaces are only reasonable in the neighborhood of the critical point, it will only be meaningful to discuss the van der Waalsian Eq. (5.2) in the critical region. We shall therefore take for the quantity A which appears in Eq. (5.2) the limiting expression (4.10) it assumes as the critical point is approached.

Moreover, the appearance in (5.2) of a second derivative with respect to the spatial coordinate makes approximation (5.2) appropriate to a continuous space rather than to a discrete space. On the other hand, the exact expression of A calculated in Section 4 is only valid for the lattice gas, not for its continuous analog. For the latter, A cannot, unfortunately, be calculated exactly in a simple closed form. However, in the approach to the critical point, the distinction between discrete and continuous spaces disappears and consequently the limiting critical expression of A for a continuous space becomes identical to that of A for a discrete space. For this reason as well as for the one given in the previous paragraph, it will only be consistent to test the approximation (5.2) with A equal to the limiting expression (4.10) it assumes as the critical point is approached.

In the ordinary van der Waals theory, phase separation is spontaneous, occurring in the absence of an external field, and in that case the term $I(m)$ in (5.2) contains the loop corresponding to the metastable and unstable portions of the subcritical isotherm. However, in our present linear model, no spontaneous phase separation can occur because the range of the interactions is finite, and a spatially nonuniform external field is required to separate the phases. But if such a field is present, then the loop of the subcritical isotherm is no longer necessary to induce phase separation: its role is now played by the field. This comparison between these two cases is illustrated in Fig. 2.

The numerical solution of Eq. (5.2) is given in Section 5.3.

5.2. Nonlinear Potential Distribution Theory

The approximate theory studied above is, like that of van der Waals which inspired it, a local theory: Equation (5.2) is the Euler–Lagrange equation deriving from a local free-energy density functional, i.e., a functional which depends on the density $\rho(z)$ [magnetization $m(z)$] and its

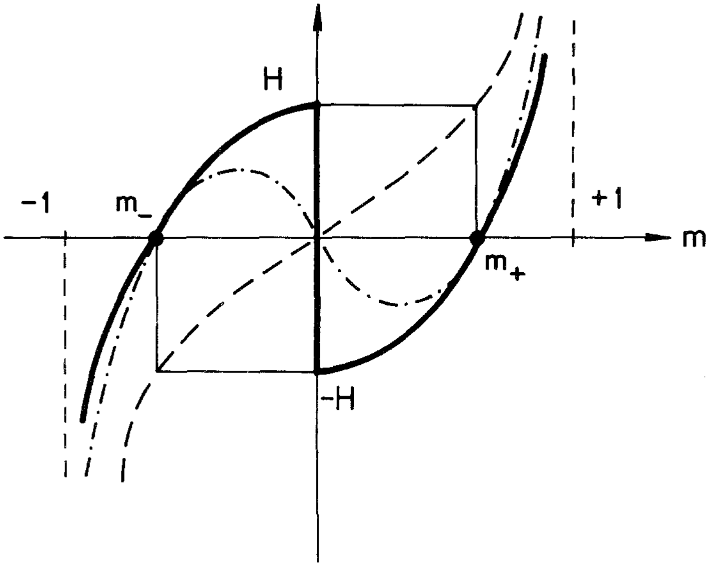

Fig. 2. Illustration of the differences between the present approximate theory (5.2) and that of van der Waals. The dashed line represents the exact isotherm $I(m)$ of the linear lattice gas and the solid line represents the function $I(m) - \mathscr{H}$, while the dotted line represents the subcritical mean-field isotherm of the van der Waals theory.

spatial gradient $(d/dz)\rho(z)$ only through their values at z and not at neighboring points z'. This local character of the free-energy density functional reflects itself in the purely local z dependence of the terms entering Eq. (5.2).

It has been shown(13) how the local van der Waals theory can be derived as a special limiting form of a more accurate nonlocal free-energy density functional. This derivation is based on the potential distribution theorem(14) which, in one dimension and in the absence of an external field, reads

$$\rho(z)/\lambda = \langle e^{-\Phi/kT}\rangle_z \tag{5.4}$$

where $\rho(z)$ is the density at z, λ is the spatially uniform thermodynamic activity and $\langle e^{-\Phi/kT}\rangle_z$ denotes the equilibrium average of $e^{-\Phi/kT}$ with Φ the energy measured by a test particle at an arbitrary fixed point z in the system.

In the presence of an external field $\mathscr{H}(z)$, Eq. (5.4) generalizes to

$$\rho(z)/\lambda = e^{-\mathscr{H}(z)/kT}\langle e^{-\Phi/kT}\rangle_z \tag{5.5}$$

In the same mean-field approximation(13) which enables one to derive the nonlocal version:

$$\varepsilon\Delta^2\rho(z) = -2\varepsilon\rho(z) + kT\ln\frac{\rho(z)}{\lambda(1-\rho(z))} \tag{5.6}$$

of what would be the van der Waals theory of the lattice-gas interface, Eq. (5.5) yields

$$\varepsilon\Delta^2\rho(z)=\mathscr{H}(z)-2\varepsilon\rho(z)+kT\ln\frac{\rho(z)}{\lambda(1-\rho(z))} \tag{5.7}$$

In Eqs. (5.6) and (5.7), $\Delta^2\rho(z)\equiv\rho(z+1)+\rho(z-1)-2\rho(z)$ is the second-difference operator while ε is the interaction energy of a pair of neighboring particles. The right-hand side of Eq. (5.7) is, apart from the external field $\mathscr{H}$, the mean-field approximation to $kT\ln[\Lambda(\rho(z))/\lambda]$, with $\Lambda(\rho)$ the activity of a lattice gas of constant density ρ. Apart from the presence of the second difference in place of the Laplacian, Eq. (5.7) is of the van der Waals type and the term in its right-hand side contains the mean-field loop.

The same observation made in Section 5.1 remains valid here: the unphysical mean-field loop contained in the right-hand side of Eq. (5.7) is made superfluous by the presence of the spatially nonuniform external field $\mathscr{H}(z)$. Therefore, just as we did in the case of the local theory presented above in Section 5.1, we shall replace Eq. (5.7) by

$$\varepsilon\Delta^2\rho(z)=\mathscr{H}(z)+kT\ln\frac{\Lambda_{\mathrm{ex}}(\rho(z))}{\lambda} \tag{5.8}$$

with $\Lambda_{\mathrm{ex}}(\rho)$ the exact activity of a linear lattice gas of constant density ρ.

The numerical solution of Eq. (5.8) is given in the following section.

5.3. Comparison With Exact Results

It will first be observed that the solutions $m(z)$ or $\rho(z)$ of the approximate equations derived above share with the exact profile the property that $m''(z)$ or $\rho''(z)$ is discontinuous at the origin $z=0$, although such a property is clearly not detectable to the eye.

The interfacial thickness ξ calculated in Section 2 is a monotone decreasing function of H/kT for fixed J/kT, in accord with a correlation inequality of Griffiths,(15) and is a monotone increasing function of J/kT for fixed H/kT.

The nonlinear differential and difference Eqs. (5.2) and (5.8) were solved numerically. For the differential Eq. (5.2) we provided the initial values $m(z=0)=0$ and $m'(z=0)$, whereas for the difference equation (5.8), $m(z=0)$ was set equal to 0 and a numerical value was given to $m(z=1)$. The value of $m'(z=0)$ or $m(z=1)$, respectively, was then varied until a solution of (5.2) or (5.8), respectively, was obtained with the desired asymptotic behavior. This procedure was first applied to a small number of

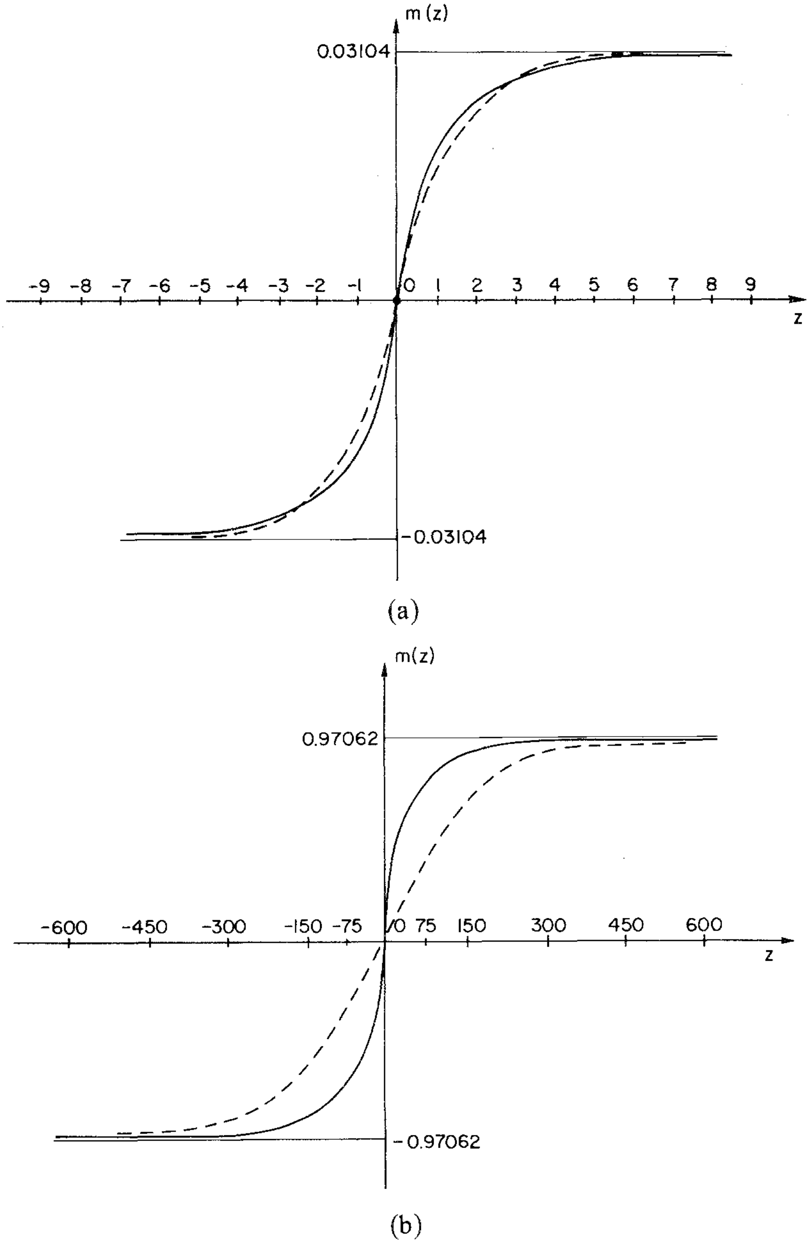

Fig. 3. (a) Exact (————) and approximate (– – – – – –) profiles for $H/kT = 0.01$ and $J/kT = 0.56661$. (b) Exact (————) and approximate (– – – – – –) profiles for $H/kT = 0.01$ and $J/kT = 3.0$.

lattice sites and was repeated for an increasingly large number until satisfactory accuracy was achieved.

Exact and approximate profiles are illustrated in Fig. 3 for a given value of H/kT and for two extreme values of J/kT appropriate to a critical and near-critical interface, i.e., values of H/kT and J/kT satisfying conditions (4.2). The local and nonlocal approximate profiles cannot be distinguished on the scale of these figures. Correspondingly a single approximate solution has been shown. It will be observed that, in accord with expectation, the agreement between the approximate and exact solutions is better the closer one is to the critical point (Fig. 3a), i.e., the better conditions (4.2) are obeyed.

6. APPROXIMATE TENSION

We now derive an analytic expression for the surface tension associated with the approximate profile derived from the corrected "barometric law" which was analyzed in Section 5.1.

As in the usual form of the van der Waals theory, we postulate the existence of a local Helmholtz free energy $\Psi(z)$; assuming that the Gibbs dividing surface is located at $z=0$, the surface tension σ is then given by[9]

$$\sigma = \int_{-\infty}^{0} [\Psi(z) - \Psi_L]\, dz + \int_{0}^{+\infty} [\Psi(z) - \Psi_G]\, dz \tag{6.1}$$

where $\Psi_L(\Psi_G)$ denotes the Helmholtz free energy of the bulk liquid (gas) phase. Integrating (6.1) by parts gives

$$\sigma = -\int_{-\infty}^{+\infty} z\Psi'(z)\, dz \tag{6.2}$$

That functional $\Psi(\{\rho\})$ which gives rise, in the variational problem of minimizing σ as given by (6.1), to the Euler–Lagrange equation (5.2), is

$$\Psi(\{\rho(z)\}) = \Psi_0(\{\rho(z)\}) + \tfrac{1}{2}A\rho'^2(z) + \mathscr{H}(z)\,\rho(z) \tag{6.3}$$

where Ψ_0 is the exact free energy of a one-dimensional lattice gas of constant density $\rho(z)$.

Inserting (6.3) into (6.2) gives

$$\sigma = -\int_{-\infty}^{+\infty} dz\, z \left[\frac{\partial \Psi_0}{\partial \rho}(z) \cdot \rho'(z) + \rho'(z)\mathscr{H}(z) + \rho(z)\mathscr{H}'(z) + A\rho'(z)\rho''(z)\right]$$

and using Equation (5.2) yields

$$\sigma = -2A \int_{-\infty}^{+\infty} dz\, z\rho'(z)\,\rho''(z) - [\mathscr{H}(+\infty) - \mathscr{H}(-\infty)] \int_{-\infty}^{+\infty} dz\, z\rho(z)\,\delta(z) \tag{6.4}$$

The last integral in (6.4) is 0, and integrating the first integral by parts gives the final result:

$$\sigma = A \int_{-\infty}^{+\infty} dz\, \rho'^2(z) \tag{6.5}$$

We observe that expression (6.5) for the surface tension is identical in form to that[9] in the van der Waals theory derived for the case when no external field is present. As the above derivation leading to (6.5) clearly shows, this coincidence is due to our special choice of the external field $\mathscr{H}(z)$, which is antisymmetric in z.

Numerical values of the surface tension σ as given by equation (6.5) for $H/kT = 0.01$ and for several values of the coupling constant J/kT are given in Fig. 4, together with the exact values of σ as given by Eq. (3.2). We observe again, as we did earlier for the density profiles, that the agreement between the approximate and exact surface tensions improves as the critical point is approached, i.e., as conditions (4.2) are more closely satisfied.

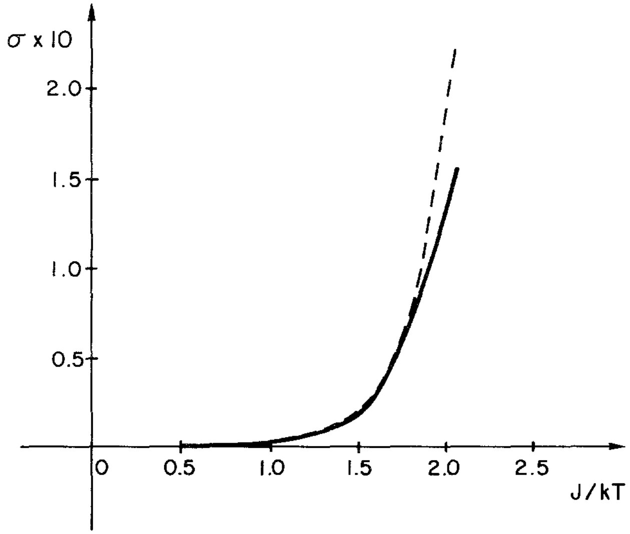

Fig. 4. Exact (————) and approximate (– – – –) surface tensions, as given by (3.2) and (6.5), respectively, for $H/kT = 0.01$ and various values of J/kT.

7. DISCUSSION

It is natural to ask to what extent the results derived here for a linear system apply to higher-dimensional systems.

Clearly it is the linear character of our lattice model of a fluid interface which enabled its density profile and surface tension to be calculated exactly. As is well known, the two-dimensional lattice-gas (Ising) model has not been solved exactly in the presence of an external field acting on all the particles (spins) of the system, even when that external field is spatially uniform.

In spite of the purely technical difficulties which still prevent an exact solution of our model to be found in more than one dimension, we expect the form of the exact result for the density profile derived in Section 2 to remain valid in any number of spatial dimensions, provided there is an external field to suppress capillary waves of wavelength greater than some capillary length.

This expectation is supported by earlier exact results on the problem of phase separation in the spherical model of the lattice gas.(1a,1b) The interface in this model was induced by an external field identical to the one we have chosen in the present model interface and it was shown that the density profile decays exponentially with a decay length equal to the correlation length of the spontaneous density fluctuations in either bulk phase.

Finally, we also expect the exact results derived here for a lattice model to remain valid for continuous systems. A remarkable difference with the discrete case discussed here is that away from the critical point, the density profile is no longer symmetric; but we expect that each wing of the density profile decays exponentially with an exponent equal to the inverse correlation length of the pure phase at the corresponding extremity of the system.

ACKNOWLEDGMENTS

One of us (M.R.) is indebted to A. Compagner for a helpful comment and is grateful to J. K. Percus for several informative and illuminating discussions, to P. Tavan for his generous advice with the computer programming, and to J. Kerins for discussions. This work was supported by the Swiss National Science Foundation, the National Science Foundation of the U.S.A., and the Cornell University Materials Science Center.

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