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LETTER TO THE EDITOR

The surface of separation between phases

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Abstract. It is proved that the interface between two coexisting pure phases in the classical lattice gas is not localised by a vanishing phase-separating field whenever the free interface is diffuse. This result is obtained for nearest neighbour, attractive interactions.

In recent years a fundamental problem has arisen in the development of theories of surface tension and of the interface between coexisting fluid phases. This is concerned with the local structure of the interface, its relationship to the surface tension and whether an intrinsic structure can be separated from shapes of the interface which vary on a scale which increases with the size of the system.

One line of theories, which culminates in that of Fisk and Widom (Fisk and Widom 1969, Widom 1972†), assumes a non-trivial density profile $\rho(x)$ in terms of which the surface tension τ is written as

$$\tau = \inf_{\rho} \int_{-\infty}^{\infty} f(\rho(x))\,\mathrm{d}x \tag{1}$$

where $f(\,.\,)$ is a local free energy density functional and the infinum is taken over a suitable class of $\rho(x)$ with boundary conditions

$$\rho(-\infty) = \rho_1 \qquad \rho(\infty) = \rho_g, \tag{2}$$

ρ_1 and ρ_g being the coexistent liquid and gas densities. The profile is required to satisfy

$$\int_{-\infty}^{\infty} x\frac{\mathrm{d}\rho}{\mathrm{d}x}(x)\,\mathrm{d}x = 0. \tag{3}$$

The functional $f(\,.\,)$ is given by the ansatz

$$f(\rho) = \psi(\rho) + A(\mathrm{d}\rho/\mathrm{d}x)^2 \tag{4}$$

where $\psi(\rho)$ is a Helmholtz free energy density analytically continued into the coexistence region. The result of (1) to (4) is a profile given by

$$2\rho(x) = \rho_1 + \rho_g + (\rho_g - \rho_1)\tanh(x/\xi) \tag{5}$$

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† This reference reviews earlier work dating to van der Waals.

where ξ, which depends on A in (4), is a length scale which, in the critical region, becomes the bulk phase correlation length.

The phenomenological theory outlined bristles with difficulties, as outlined by Widom (1972). One is the apparent disagreement with fundamental theories for lattice gases and their Ising spin isomorphs, for which a satisfactory macroscopic definition of surface tension is obtained, but with vanishing density profile $\rho(x)$; this will now be described.

Consider a rectangular lattice Λ in d dimensions centred on the origin with a spin variable $\sigma(x)=\pm 1$ at each point $x=(x_1,\ldots x_d)$ of the lattice. The x_j are integers satisfying $-N\leqslant x_j\leqslant N$ for $j=1,\ldots d-1$, but $-M+1\leqslant x_d\leqslant M$. The energy of a configuration of spins is taken to be

$$E_\Lambda(\{\sigma\})=-J\sum_{|i-j|=1}\sigma(i)\sigma(j)-\sum \tilde{h}(i)\sigma(i). \tag{6}$$

The fields $\tilde{h}(i)$ which act on the spins on the boundary $\partial\Lambda$ of Λ may be classified as boundary conditions b_Λ as follows:

$b_\Lambda=++$: $\tilde{h}(i)=+\infty$ on $\partial\Lambda$,

$b_\Lambda=+-$: $\tilde{h}(i)=+1$ (respectively $-\infty$) if $i_d+\frac{1}{2}>0$ (respectively <0) on $\partial\Lambda$,

$b_\Lambda=f$: $\tilde{h}(i)=0$ on $\partial\Lambda$,

$b_\Lambda=c$ if the lattice is cylindrical

with axis $(0,\ldots 0,1)$ and $\tilde{h}(i)\geqslant 0$ on the ends.

A natural candidate for surface tension is (Camp and Fisher 1972, Abraham *et al* 1973, Abraham and Martin-Löf 1973, Abraham and Reed 1974, 1976, Abraham 1978)

$$\tau=\lim_{n\to\infty}\frac{1}{(2N+1)^{d-1}}\lim_{M\to\infty}\log\left(Z_\Lambda(+-)/Z_\Lambda(++)\right) \tag{7}$$

where $Z_\Lambda(b_\Lambda)$ is the partition function for boundary condition b_Λ with $\tilde{h}(i)=0$ at all interior points. Such a surface tension exists (Gruber *et al* 1977) and has been evaluated when $d=2$ (Abraham *et al* 1973, Abraham and Reed 1974, 1976) agreeing with Onsager's (1944) result.

Consider fields $\tilde{h}(i)$ defined at interior points of Λ by

$$\tilde{h}((i)_{d-1},i_d)=-\tilde{h}((i)_{d-1},-i_d) \tag{8}$$

$$\tilde{h}((i)_{d-1},i_d)=h\geqslant 0 \qquad \text{for } i_d\geqslant 0. \tag{9}$$

Define a profile function by

$$F(p;h,\Lambda,b_\Lambda)=\langle\sigma(p)\rangle\Lambda,\tilde{h},b_\Lambda \tag{10}$$

with $\tilde{h}$ defined as in (8) and (9).

Several results have been obtained for $F(p;0,\infty,+-)$, which is the density profile. For $d=2$ (Abraham and Reed 1974, 1976) the profile always vanishes, at total apparent variance with the Fisk–Widom result. For $d=3$ it has been proved that, for

$T < T_c(2)$ where $T_c(d)$ is the d-dimensional critical temperature, the profile is non-vanishing (van Beijeren 1975). But convincing evidence has been given for $T_R < T < T_c(3)$ that the profile again vanishes (Weeks *et al* 1973). Here $T_R \sim T_c(2)$, which should be compared with phenomenological ideas (Burton *et al* 1951). Such a vanishing of the magnetisation profile has been termed roughening.

A possible interpretation of these results is that the interface has an intrinsic structure, quite possibly given by theories of Fisk–Widom type, carried by uncoupled long-wavelength capillary waves which give a divergent amplitude at the interior of Λ as in the drumhead model (Widom 1972). These capillary waves average the magnitisation profile to zero. A fundamental question is whether the profile can be localised by using an external field $\tilde{h}$ to damp the capillary waves.

We have proved the following.

Theorem

$$\lim_{\Lambda\to\infty} F(p; h, \Lambda, +-) = F(p; h, +-) \tag{11}$$

exists for any $h \geq 0$ with $\Lambda \to \infty$ in the sense of van Hove:

$$\lim_{h\to 0+} F(p; h, +-) = F(p; 0, +-) \tag{12}$$

$$0 \leq \lim_{h\to 0+} F(p; h, c) \leq F(p; 0, +-) \tag{13}$$

$$0 \leq \lim_{h\to 0+} F(p; h, f) \leq F(p; 0, +-). \tag{14}$$

This implies that localisation of a roughened interface is not achieved as $h \to 0$.

The method of proof uses van Beijeren's inequalities (van Beijeren 1975) and the techniques of Martin-Löf (1972) and of Lebowitz and Martin-Löf (1972), Lebowitz (1974) and Percus (1975). If the field term in (6) is rewritten

$$\sum_{i_d\geq 0} \sum_{(i)_{d-1}} \tilde{h}(i)[\sigma((i)_{d-1}, i_d) - \sigma((i)_{d-1}, -i_d] \tag{15}$$

then $\langle\sigma(p)\rangle$ for $p_d \geq 0$ is non-negative and non-decreasing as any $\tilde{h}(i)$ increases. We then have

$$F(p; h, \Lambda_1, +-) \geq F(p; h, \Lambda_2, +-) \geq 0$$

for any $\Lambda_2 > \Lambda_1$. This gives (11). Also

$$F(p; h, \Lambda, +-) \geq F(p; h, +-).$$

Thus

$$\lim_{h\to 0+} \sup F(p; h, +-) \leq F(p; 0, +-).$$

But

$$F(p; h, \Lambda, +-) \geq F(p; 0, \Lambda, +-)$$

for any Λ. Hence

$$\lim_{h\to 0+} \inf F(p; h, +-) \geq F(p; 0, +-)$$

and (12) is proved. Equations (13) and (14) are obtained by noting that $b_\Lambda = +-$ is obtained by increasing $h(i)$ for $i \in \partial\Lambda$ in (15) from both $b_\Lambda = f$ and $b_\Lambda = c$.

Localisation will certainly be achieved when $h > 0$ in (10) and $\Lambda \to \infty$, and will vanish asymptotically as $h \to 0$, presumably with a new length scale diverging as $h \to 0$.

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