Effective Forces Induced by a Fluctuating Interface: Exact Results

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We present exact derivations of the effective capillary wave fluctuation-induced forces resulting from pinning of an interface between two coexisting phases at two points separated by a distance r. In two dimensions the Ising ferromagnet calculations based on the transfer matrix approach give an attractive force decaying as $1/r$ for large distances. In three dimensions mapping of the body-centered solid-on-solid model onto the 6-vertex model allows for exact solution using the bosonization analysis of the equivalent XXZ Heisenberg quantum chain. The exact result gives the attractive force which decays asymptotically as $1/(r \log r)$.

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Interfaces between coexisting thermodynamic phases exhibit large spatial fluctuations at temperatures above the roughening transition. The length scale of such fluctuations diverges with system size, so that the interface is ''washed out'' in the thermodynamic limit (unless suitable external fields are applied), a result completely at variance with classical thermodynamical expectations. Nevertheless, such a striking phenomenon has recently been observed by a direct visual method in an ingeniously constructed experiment with a colloidal system [1]. Further, there are many implicit manifestations in such diverse areas as biological systems [2], the asymptotic behavior of correlation functions [3], and vicinal sections of crystals in the terrace-ledge-kink (TLK) model [4,5]. Here ledge fluctuations are examined, typically when there is a short range interaction between such ledges, either attractive or repulsive, together with a long-ranged repulsion which comes about because neighboring ledges cannot cross and so restrict each others' configuration space. Such a force is said to be of ''entropic'' or ''Casimir'' type. A crucial fact, which will be used later in another context, is that the TLK model of a crystal surface can be mapped onto the 6-vertex model of Lieb [6] and solved exactly, with various phase transitions resulting, depending on the nature of the short-ranged force: attraction gives surface reconstruction, repulsion facet selection at a ''magic'' angle, with the facet disappearing by a roughening mechanism. In this Letter we consider a related interfacial problem, but one in which geometric limitation of the configuration of the interface manifests itself in a long range attraction. This we analyze in $d = 2$ and $d = 3$ by using exact $d = 2$ Ising techniques in the former case and another 6-vertex mapping, together with some new results, in the latter case. This 6-vertex mapping, due to van Beijeren [7], is different from the TLK one, but has the crucial common feature that it gives height conservation around closed loops, a necessary condition for the integrity of the surface. Further, it manifests a phase transition of roughening type [8].

It is well known that chemicophysical forces can trap colloidal particles at the liquid-liquid or liquid-vapor interface at coexistence [9]. This phenomenon is widely used, for example, to create the stable emulsions in systems called Pickering emulsions [10]. Another scenario here is that of a bifunctional particle, say a sphere, the surface of which is divided at the equator into two hemispheres with differential wetting properties. Since the colloidal particles are much larger and more massive than the ones in the phase separating systems, they restrict the motion of the interface to which they are rigidly attracted strongly. As a limiting case, they can be treated as spatially fixed. The phase space restriction then implies, as we shall show later, that, were the massive particles to be released, then they would accelerate toward each other. The interest of such questions stems not only from the various practical applications [9,11,12] but also from the basic requirement to understand the nature of the effective forces between the colloidal particles [13,14]. In particular, the important role of the aforementioned capillary fluctuations is clear. Substantial progress has recently been made [15,16], but there remain a number of issues.

First, we calculate the incremental free energy of an interface in the $d = 2$ Ising ferromagnet resulting from pinning, which in this case can be achieved in various ways. The method, which carries over to our $d = 3$ calculations, is to fix the interface at its extremities and to use this for the reference state. The pinned state is then a further restriction of the reference state in which two interior points are required to have the same interface displacement, but all such displacements are allowed with equal weight. The associated partition functions are calculated using the standard transfer matrix technique, supplemented with the ''domain wall state method'' [17]: the state $|m\rangle$ achieves localization at the position m on any

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line normal to the mean interface direction and can be written as

$$|m\rangle = M^{-1/2}\sum_k \exp[-ik(m+1/2)]G^\dagger(k)|\Phi\rangle. \quad (1)$$

Here $|\Phi\rangle$ is both the $G(k)$ vacuum and the maximal eigenvector of the transfer matrix V. The $G^\dagger(k)$ are Fermi operators which "diagonalize" the transfer matrix for a lattice of width M normal to the transfer direction [18]. Thinking of the transfer matrix as generating a discrete Euclidean time evolution, the $G^\dagger(k)$ create "particles" with energy $\gamma(k)$ given by Onsager's formula [19] $\cosh\gamma(k) = \cosh 2K \cosh 2K^* - \cos k$, where K is the nearest-neighbor coupling in units of k_BT, K^* is the dual coupling given by the involution $\sinh(2K)\sinh(2K^*) = 1$. It is important to note that $|m\rangle$ only localizes the interface up to the bulk correlation length as is revealed by calculating the local magnetization [17]. The ratio of the partition function with two pinned states $|m\rangle$ separated by a horizontal distance $2n$ (see Fig. 1), denoted by $Z^\times(n|N,M)$ to that for the unpinned system, denoted by $Z(N,M)$, is

$$\frac{Z^\times(n|N,M)}{Z(N,M)} = \frac{1}{\langle 0|V^{2N}|0\rangle}\sum_m \langle 0|V^{N-m}|m\rangle\langle m|V^{2n}|m\rangle \times \langle m|V^{N-m}|0\rangle. \quad (2)$$

As $M \to \infty$, bringing in expression for $\langle m|$ gives

$$\frac{Z^\times(n|N,\infty)}{Z(N,\infty)} = \sum_m \frac{[U(N-n,m)]^2 U(2n,m)}{U(2N,0)}, \quad (3)$$

where

$$U(N,m) = \int_0^{2\pi}\frac{d\omega}{2\pi} e^{-N\gamma(\omega)+im\omega}. \quad (4)$$

Evaluating the sum over m in (3) gives

$$\frac{Z^\times(n|N,\infty)}{Z} = \frac{U(2N-2n,0)U(2n,0)}{U(2N,0)}. \quad (5)$$

Finally, using the fact that

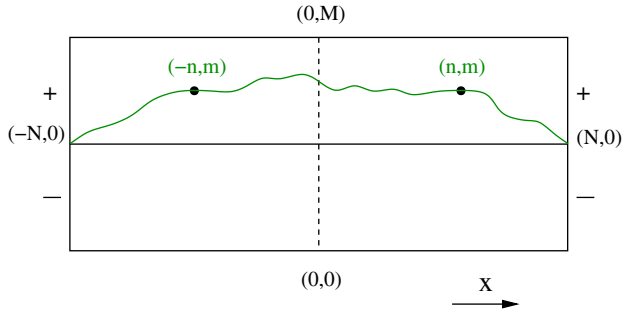

FIG. 1 (color online). Schematic plot of Ising lattice with interface pinned by its end points and in two interior points at the same level. The nearest-neighbor ferromagnetic coupling is K in units of kT. The transfer matrix acts in the x direction.

$$\lim_{N\to\infty}\frac{U(2N-2n,0)}{U(2N,0)} = e^{-2n\gamma(0)}, \quad (6)$$

we conclude that in the limit $M, N \to \infty$ the incremental free energy is given by

$$\beta f^\times(n) = -\log\left[\int_0^{2\pi}\frac{d\omega}{2\pi} e^{-2n[\gamma(\omega)-\gamma(0)]}\right]. \quad (7)$$

Here $\gamma(0)$ is proportional to the inverse correlation length. The asymptotics for large n of this are determined by the Laplace method

$$\beta f^\times \sim \log\sqrt{2\pi\gamma^{(2)}(0)r/a_0} + \mathcal{O}(1), \quad (8)$$

where $r = 2na_0$ and a_0 is the lattice spacing, valid for $n\gamma^{(2)}(0) \gg 1$, i.e., $r \gg a_0/\gamma^{(2)}(0)$, where $1/\gamma^{(2)}(0)$ is the interface stiffness. The stiffness comes in because the surface tension is angle dependent on the lattice. The question of angle dependence of (8) will be discussed elsewhere. The implied force is

$$\mathcal{F}(r) \sim -\frac{kT}{2}\frac{1}{r}. \quad (9)$$

Notice that the law itself does not depend on the stiffness, or on surface tension, but the range of validity does. Techniques like those in Ref. [1] might be used to make the lower bound on r as small as possible. The reader might feel that the pinning mechanism is somewhat contrived. If the interface were localized both at the boundaries and at both the interior points, perhaps a more intuitive restriction than "floating" at the same level, then $Z^\times/Z \to 0$ as $N \to \infty$, rendering the definition useless. In experiments one always has a finite system, which may introduce an additive term in (7), which is independent of n, but which may well diverge with N, as would be the case with the alternative pinning just described. But for any finite N, this would not come up in the force as in (9). There are many variants here, which will be developed in a longer paper.

We turn now to $d = 3$ and consider the van Beijeren body-centered-cubic solid-on-solid (BCSOS) [7] model, where height changes are associated with vertex configurations, as shown in Fig. 2. The fact that the allowed

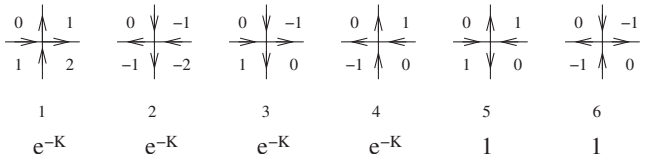

FIG. 2. The arrow configurations of allowed configurations of the 6-vertex model. The rule for associating plaquette heights on the dual lattice is that, pointing along the arrow, the plaquette on the right is higher. Vertices 1 to 4 have a diagonal height change in one or the other direction. Vertices 5 and 6 have a ripple (no diagonal height change) and are deemed to be flat. The weight assignment, with $K > 0$, favors rippling over diagonal height change.

configurations are those of the 6-vertex model with two arrows in and two arrows out guarantees height conservation around any close loop, which is required for the integrity of the sheet. Along the $(1,0)$ direction, which is normal to the transfer direction, the height difference of abutting plaquettes is strictly ± 1. Labeling the row of vertical arrows by eigenvalues of $2S_j^z$ for spin $-1/2$, the following XXZ Heisenberg-Ising Hamiltonian,

$$\mathcal{H}_{XXZ} = J\sum_{j=1}^{M}[(S_j^x S_{j+1}^x + S_j^y S_{j+1}^y) + \Delta S_j^z S_{j+1}^z], \quad (10)$$

$S_{M+1}^{\alpha} = S_1^{\alpha}$, $\alpha = x, y, z$ (cyclic boundary conditions) commutes with the transfer operator, provided $\Delta = 1 - (1/2)e^K$. Thus $-\infty < \Delta < 1/2$. The region of interest here is for $-1 < \Delta < 1/2$ where the interface is rough. The ground state of (10) furnishes the maximum eigenvalue of the transfer matrix. Proceeding in the $(1,0)$ direction, the height difference at a separation $r = 2na_0$ for integer n is

$$\delta h = 2\sum_{j=1}^{2n} S_j^z. \quad (11)$$

In this Letter, we are interested in the situation when $\delta h = 0$. The ratio of partition function with this height fixing to that without it is

$$\frac{Z^{\times}(n)}{Z} = \int_0^{\pi}\frac{d\theta}{\pi} f(\theta, 2n) = e^{-\beta f^{\times}(n)}, \quad (12)$$

where $f^{\times}(n)$ is the associated incremental free energy and

$$f(\theta, 2n) = \left\langle \exp\left(i\theta\sum_{j=1}^{2n} S_j^z\right)\right\rangle_{\mathcal{H}_{XXZ}}. \quad (13)$$

We are interested in the large-n asymptotics of $f(\theta, 2n)$. We note that $\exp(-\beta f^{\times}(n))$ is simply the probability that the z component of the spin on the interval $[1, 2n]$ is zero. In this sense this quantity is related to Korepin's "emptiness formation probability" and its generalizations [20,21]. To calculate $\exp(-\beta f^{\times}(n))$ we employ a bosonization analysis.

It is well known that the large distance behavior of correlation functions in the Heisenberg-Ising model (10) is described by a Gaussian model [22]

$$\mathcal{H} = \frac{1}{16\pi}\int dx\left[v(\partial_x\Phi)^2 + \frac{1}{v}(\partial_t\Phi)^2\right]. \quad (14)$$

Here the scalar field Φ is compact $\Phi(x) \equiv \Phi(x) + 8\pi\alpha$, and the velocity v and compactification radius 4α are given in terms of the parameters of the lattice Hamiltonian (10) and the lattice spacing a_0 as $\alpha = (\arccos(-\Delta)/4\pi)^{(1/2)}$, and $v = (Ja_0\sin(4\pi\alpha^2))/(2(1-4\alpha^2))$. The lattice spin operator S_j^z is expressed in terms of the bosonic field as

$$S_j^z \sim \frac{a_0}{8\pi\alpha}\partial_x\Phi(x) - A(-1)^j a_0^{1/8\alpha^2}\sin\left(\frac{\Phi(x)}{4\alpha}\right) + \cdots, \quad (15)$$

where $x = ja_0$ and A is a known constant [23]. We now turn to the bosonization of $\exp(i\theta\sum_{j=1}^n S_j^z + \frac{1}{2})$. We first note that this operator is a 2π-periodic function of θ, which allows us to write

$$f(\theta, n) = \frac{e^{-in\theta}}{2}[\langle e^{i\theta\Sigma_{j=1}^n (S_j^z + 1/2)}\rangle_{\mathcal{H}_{XXZ}} + \langle e^{i(\theta-2\pi)\Sigma_{j=1}^n (S_j^z+1/2)}\rangle_{\mathcal{H}_{XXZ}}]. \quad (16)$$

Application of (15) then gives (the staggered part of S_j^z does not contribute to the sum as $\Phi(x)$ is a slowly varying field)

$$e^{i\theta\Sigma_{j=1}^n S_j^z} \sim A(\theta)\exp\left(\frac{i\theta}{8\pi\alpha}\int_0^{na_0} dx\partial_x\Phi\right) = A(\theta)\exp\left(\frac{i\theta}{8\pi\alpha}[\Phi(na_0) - \Phi(0)]\right). \quad (17)$$

Here $A(\theta)$ is a normalization constant. The expectation value of (17) is easily calculated

$$\langle e^{i\theta\Sigma_{j=1}^n S_j^z}\rangle_{\mathcal{H}} \sim A(\theta)(nc)^{(\theta/4\pi\alpha)^2}, \quad (18)$$

where $c^{-1}a_0$ is a short-distance cutoff. Using this result we obtain the following expression for $f(\theta, n)$:

$$f(\theta, n) \sim \frac{A(\theta)}{2}(mc)^{-(\theta/4\pi\alpha)^2} + (-1)^n\frac{A(\theta-2\pi)}{2}(nc)^{-[(\theta-2\pi)/4\pi\alpha]^2}. \quad (19)$$

We can check (19) by comparing it to the known expression at the free fermion point $\Delta = 0$. Here $f(\theta, n)$ can be expressed as a Toeplitz determinant; see [18,24] and references therein. The large-n asymptotics have been calculated in [25] with the result

$$f(\theta, n) = \frac{a(\theta)}{(2n)^{\theta^2/2\pi^2}} + (-1)^n\frac{a(1-\theta)}{(2n)^{(\theta-2\pi)^2/2\pi^2}}, \quad (20)$$

where

$$a(\theta) = \exp\left(\frac{\theta^2}{2\pi^2}\int_0^{\infty}\frac{dt}{t}\left[e^{-2t} - \frac{4\pi^2}{\theta^2}\frac{\sinh^2(\theta t/2\pi)}{\sinh^2(t)}\right]\right). \quad (21)$$

This agrees with the general expression (19). It is now a simple matter to calculate $\exp(f^{\times}(2n))$, as for large n the θ integral is dominated by its saddle point. Hence

$$e^{-\beta f^{\times}(n)} \sim \frac{\mathcal{A}}{\sqrt{\log(nc')}}, \quad (22)$$

where $\mathcal{A}$ and c' are (Δ-dependent) constants. Thus, the resulting force is attractive and behaves for large r as

$$\mathcal{F}(r) \sim -\frac{kT}{2r\log(rc'/a_0)}. \quad (23)$$

Notice the difference between (22) and (9).

In this Letter, we have presented exact calculations of the incremental free energy resulting from pinning the interface between two coexisting phases at two points separated by a distance r. The case for $d = 2$ is more detailed because it allows the interface to have a diffusive structure at the molecular level, as is known to be the case in real systems. The resulting force is attractive with a remarkably long-ranged decay as $1/r$. In $d = 3$, we have treated this pinning phenomenon within the BCSOS model of a random surface, using van Beijeren's isomorphism with the 6-vertex model. Thus, the interface is locally sharp. It is defined at points on a Z^2 square lattice. The attractive force in this case does not differ strongly from the $d = 2$ one, in that it decays as $1/(r\log r)$ instead of as $1/r$, a rather striking result. Note that these forces are of much longer range than the electrostatic ones induced by photon fluctuations, termed van der Waals [26] or the fluctuation-induced Casimir-type repulsion between extended objects in similar systems. This $1/(r\log r)$ result has also been obtained by Lehle, Oettel, and Dietrich [16] in a continuum model for a particular, but very physically reasonable, case of contact of the interface with two extended objects; these we may think of as spheres each with two hemispherical surfaces having different wetting properties which keep the sphere at the interface at an orientation and immersion which makes the equatorial line separating the two wetting regions sit exactly in the interface, as mentioned at the beginning of this Letter. The case we have considered is an extreme one in that the colloidal sphere has been treated as though it were a point (or a unit cube on the dual lattice). In mitigation, our results for $d = 3$ are obtained for mesoscopic modeling which retains, unlike the usual capillary wave scenarios, molecular scale discreteness and which also shows a roughening transition.

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