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Correlations at a liquid–gas interface: asymptotic analysis for weak gravity

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Abstract. Density-density correlation functions at the phase-separating layer in a two-dimensional solid-on-solid lattice model are studied. We perform for weak gravitational fields an exact asymptotic analysis and obtain explicit expressions. A recent numerical analysis by Stecki and Dudowicz is shown to be in good agreement with our exact expansion.

1. Introduction

There is an increasing interest in the equilibrium properties of spatially non-uniform fluids, particularly of those of interfaces between fluid phases (Croxton 1980, Rowlinson and Widom 1982, Bedeaux 1986). In the microscopic theory of non-uniform classical fluids an essential role is played by the correlation functions and it is of interest to study the decay of correlations both along the interface and orthogonal to the phase-separating layer.

Few models are amenable to exact analysis. To obtain simple and transparent results it is a natural idea to use the solid-on-solid version of the two-dimensional lattice gas and this is the model we study. Fluctuations of the interface are particularly strong in two-dimensional systems: the zero-gravity interface is rough at all temperatures. An external field, i.e. the gravitational field, has two effects: it localises the average position of the interface in space and it reduces the fluctuations of the interface about this average position. Gravity is a very weak force, and it is natural to ask whether one can perform an exact asymptotic expansion of physical quantities when the gravitational constant g is assumed to be small. In an interesting recent paper, which served as a motivation for the present investigation, Stecki and Dudowicz (1986) studied precisely such an expansion by numerical means. We will demonstrate in the present paper that an analytical treatment is feasible. Explicit low-order results for the interface density profile, the height-height correlation function, the density-density correlation function and the local susceptibility are given. In most cases the numerical results of Stecki and Dudowicz (1986) are found to be in good agreement with our exact expansions.

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2. The model

The surface between an upper gas phase of density ρ_g and a lower liquid phase of density ρ_l can, in the lattice model, be described by a set $\{h_i\}$ of integer heights. The Hamiltonian is of nearest-neighbour type:

$$H\{h_i\} = 2J \sum_{i=1}^{L} |h_i - h_{i+1}| + \tfrac{1}{2}mg(\rho_l - \rho_g) \sum_{i=1}^{L} (h_i - h_0)^2. \tag{1}$$

The constant h_0 determines the average height of the phase-separating layer, and it is no restriction to take $h_0 = 0$. An arbitrary constant in H is omitted. This constant includes the nearest-neighbour interaction energy

$$E_0 = 2JL \tag{2}$$

for a flat surface, as well as a possible constant field energy contribution.

The height coordinates h_i are assumed unrestricted (restricting the heights to a finite range localises the interface and is in several respects similar to localisation by a finite gravitational field, as shown by Stecki *et al* (1986)). It is convenient to assume periodic boundary conditions along the interface, $h_{i+L} = h_i$, and the limit $L \to \infty$ is to be taken.

The probability distribution $P(\{h_i\})$ of an interface configuration is given by the Boltzmann factor

$$P(\{h_i\}) = Z^{-1} \exp(-\beta H) \tag{3}$$

with

$$Z = \sum_{\{h_i\}} \exp(-\beta H)$$

the partition function.

P can be expressed in terms of a symmetric transfer matrix

$$T(h_i, h_j) = \exp(-2K|h_i - h_j| - \tfrac{1}{2}Gh_i^2 - \tfrac{1}{2}Gh_j^2). \tag{4}$$

Here

$$G = \tfrac{1}{2}gm(\rho_l - \rho_g)\beta \qquad K = \beta J \tag{5}$$

with $\beta^{-1} = k_B T$ being the product of the Boltzmann constant and the absolute temperature. Explicitly we have

$$P(\{h_i\}) = Z^{-1} \prod_{i=1}^{L} T(h_i, h_{i+1}) \tag{6}$$

and

$$Z = \sum_h (T^L)_{hh}. \tag{7}$$

3. The eigenvalue problem

All physical quantities can be conveniently expressed in terms of eigenvectors ψ_n and eigenvalues λ_n of the transfer matrix:

$$T\psi_n = \lambda_n \psi_n \qquad \lambda_0 \geqslant \lambda_1 \geqslant \lambda_2 \geqslant \ldots . \tag{8}$$

Since T is real and symmetric, the eigenvectors can be chosen to be real, and the positivity of the matrix elements ensures that the maximum eigenvalue λ_0 is positive.

The eigenvalue problem (8) is easily turned into the simple recursion

$$\exp[\tfrac{1}{2}G(h+1)^2]\psi(h+1)+\exp[\tfrac{1}{2}G(h-1)^2]\psi(h-1) = [2\cosh 2K - 2\lambda^{-1}\sinh 2K \exp(-Gh^2)]\exp(\tfrac{1}{2}Gh^2)\psi(h) \tag{9}$$

using the identity

$$\exp(-2K|n+1|)+\exp(-2K|n-1|) = 2\cosh 2K \exp(-2K|n|) - 2\sinh 2K\delta_{n0}. \tag{10}$$

The recursion (9) has the form of a discrete Schrödinger equation for

$$\hat{\psi}(h) = \psi(h)\exp(\tfrac{1}{2}Gh^2) \tag{11}$$

with a potential that becomes slowly varying for small G. This motivates the perturbation expansion (van Leeuwen and Hilhorst 1981).

We prepare for the perturbation expansion by putting

$$\psi(h\pm 1) = \exp(\pm \mathrm{d}/\mathrm{d}h)\psi(h) \tag{12}$$

by scaling heights through

$$\gamma h = y \qquad \psi(h) = \sqrt{\gamma}\phi(y) \tag{13}$$

and by introducing a scaled eigenvalue parameter

$$\Lambda = (\lambda \tanh K)^{1/2}. \tag{14}$$

In terms of these variables equation (9) takes the form

$$(\mathrm{e}^{Gy/\gamma}\,\mathrm{e}^{\gamma\mathrm{d}/\mathrm{d}y} + \mathrm{e}^{-Gy/\gamma}\,\mathrm{e}^{-\gamma\mathrm{d}/\mathrm{d}y} - 2\,\mathrm{e}^{-G/2})\phi(y) = 4\,\mathrm{e}^{-G/2}\sinh^2 K\,(1-\Lambda^{-2}\,\mathrm{e}^{-y^2G/\gamma^2})\phi(y). \tag{15}$$

The appropriate scaling of the stretching variable γ is $\gamma \propto G^{1/4}$ and it will be convenient to take

$$\gamma = (2\sinh K)^{1/2}G^{1/4} \tag{16}$$

in order to simplify later expressions. Equation (15) can now be expanded in powers of $G^{1/2}$. As expansion parameter we introduce

$$\varepsilon = \tfrac{1}{2}G^{1/2}/\sinh K \tag{17}$$

rather than G itself. This assumes that the expansion is performed at a fixed finite temperature. The final form of the exact recursion (15) is then

$$\Omega\phi(y) = 0 \tag{18}$$

with

$$\Omega = -\tfrac{1}{8}\varepsilon^{-1}S^{-2}[\exp(2S\varepsilon^{3/2}y)\exp(\varepsilon^{1/2}\mathrm{d}/\mathrm{d}y) + \exp(-2S\varepsilon^{3/2}y)\exp(-\varepsilon^{1/2}\mathrm{d}/\mathrm{d}y) - 2\exp(-2S^2\varepsilon^2)] + \tfrac{1}{2}\varepsilon^{-1}\exp(-2S^2\varepsilon^2)[1-\Lambda^{-2}\exp(-\varepsilon y^2)] \tag{19}$$

in which we have introduced the abbreviation

$$S \equiv \sinh K. \tag{20}$$

So far everything is exact. We now expand

$$\Omega = \Omega^{(0)} + \varepsilon\Omega^{(1)} + \ldots \tag{21}$$

$$\phi = \phi^{(0)} + \varepsilon\phi^{(1)} + \ldots \tag{22}$$

$$\Lambda = 1 + \varepsilon\Lambda^{(1)} + \varepsilon^2\Lambda^{(2)} + \ldots \tag{23}$$

and find

$$\Omega^{(0)} = -\tfrac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2} + \tfrac{1}{2}y^2 + \Lambda^{(1)} \tag{24}$$

$$\Omega^{(1)} = -\tfrac{1}{6}S^2\frac{\mathrm{d}^4}{\mathrm{d}y^4} - \tfrac{1}{4}y^4 - \Lambda^{(1)}y^2 - y\frac{\mathrm{d}}{\mathrm{d}y} - \tfrac{3}{2}\Lambda^{(1)2} - \tfrac{1}{2} + \Lambda^{(2)}. \tag{25}$$

To lowest order

$$\Omega^{(0)}\phi^{(0)} = \left(-\tfrac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2} + \tfrac{1}{2}y^2 + \Lambda^{(1)}\right)\phi^{(0)} = 0 \tag{26}$$

which is a harmonic oscillator Schrödinger equation. Thus

$$\Lambda_n^{(1)} = -n - \tfrac{1}{2} \qquad n = 0, 1, 2, \ldots. \tag{27}$$

Using the corresponding eigenstates $|n\rangle$ as a basis, we have to next order

$$\langle n|\Omega^{(1)}|n\rangle = 0. \tag{28}$$

This determines $\Lambda_n^{(2)}$. A straightforward evaluation of the left-hand side of (28) yields

$$\Lambda_n^{(2)} = \tfrac{7}{8}n(n+1) + \tfrac{5}{16} + \tfrac{1}{4}S^2(n^2 + n + \tfrac{1}{2}). \tag{29}$$

The dominating corrections to the zero-order eigenfunctions $\phi_n^{(0)}(y) \equiv \langle y|n\rangle$ are also obtainable by standard perturbation theory. The form of the perturbation (25) shows that the only non-vanishing terms are

$$\phi_n^{(1)} = \alpha_{n,n+4}\phi_{n+4}^{(0)} + \alpha_{n,n+2}\phi_{n+2}^{(0)} + \alpha_{n,n-2}\phi_{n-2}^{(0)} + \alpha_{n,n-4}\phi_{n-4}^{(0)}. \tag{30}$$

Explicit evaluation yields

$$\begin{aligned}
\alpha_{n,n+4} &= -\frac{2S^2+3}{192}[(n+1)(n+2)(n+3)(n+4)]^{1/2} \\
\alpha_{n,n+2} &= -\frac{2S^2+3}{24}(n+\tfrac{3}{2})[(n+1)(n+2)]^{1/2} \\
\alpha_{n,n-2} &= \frac{2S^2+3}{24}(n-\tfrac{1}{2})[(n-1)n]^{1/2} \\
\alpha_{n,n-4} &= -\frac{2S^2+3}{192}[(n-3)(n-2)(n-1)n]^{1/2}.
\end{aligned} \tag{31}$$

The eigenvalues λ_n of the transfer matrix follow now from (14), (27) and (29):

$$\lambda_n = \Lambda_n^2 \coth K = \coth K[1 + \varepsilon\lambda_n^{(1)} + \varepsilon^2\lambda_n^{(2)} + \mathcal{O}(\varepsilon^3)] \tag{32}$$

with

$$\lambda_n^{(1)} = -2n - 1 \tag{33}$$

$$\lambda_n^{(2)} = \tfrac{11}{4}n(n+1) + \tfrac{7}{8} + \tfrac{1}{2}S^2(n^2 + n + \tfrac{1}{2}). \tag{34}$$

The principal eigenfunction

$$\phi_0(y) = \pi^{-1/4} \exp(-\tfrac{1}{2}y^2)[1 + \varepsilon(2S^2+3)(\tfrac{1}{48}y^4 - \tfrac{3}{16}y^2 + \tfrac{5}{64}) + \mathcal{O}(\varepsilon^2)] \tag{35}$$

will be particularly important in the following.

The ratio of two eigenvalues will be close to unity, and the small quantity

$$\kappa_n = \ln(\lambda_0/\lambda_n) \tag{36}$$

which will be useful below, has the following expansion:

$$\begin{aligned}\kappa_n &= \varepsilon(\lambda_0^{(1)} - \lambda_n^{(1)}) + \varepsilon^2(\lambda_0^{(2)} - \lambda_n^{(2)} - \tfrac{1}{2}\lambda_0^{(1)^2} + \tfrac{1}{2}\lambda_n^{(1)^2}) + \mathcal{O}(\varepsilon^3) \\ &= 2n\varepsilon - (\tfrac{1}{2}S^2 + \tfrac{3}{4})n(n+1)\varepsilon^2 + \mathcal{O}(\varepsilon^3).\end{aligned} \tag{37}$$

4. Density profile

The probability $p(h)$ that column number n has *precisely* height h is

$$p(h) = \sum_{\{h_i\}} \delta_{h_i h} P\{h_i\} = \frac{(T^L)_{hh}}{\sum_h (T^L)_{hh}} = \frac{\sum_n \lambda_n^L \psi_n^2(h)}{\sum_n \lambda_n^L} \simeq \psi_0^2(h). \tag{38}$$

The configuration probability P has been expressed in terms of the transfer matrix; we have used the expansion in terms of eigenvectors

$$T(h, h') = \sum_n \lambda_n \psi_n(h)\psi_n(h') \tag{39}$$

the orthogonality of the eigenvectors, and have, in the last step, taken the limit $L \to \infty$.

The average density $\rho(z)$ at a height z is determined by the probability that an arbitrary column has a height $h \geq z$:

$$\rho(z) = \rho_g + (\rho_l - \rho_g) \sum_{h=z}^{\infty} p(h). \tag{40}$$

Since the expansion treats the heights as continuous variables we convert the sum to an integral by a convenient version of the Euler-Maclaurin summation formula (appendix 1):

$$\sum_{h=z}^{\infty} p(h) = \int_{z-1/2}^{\infty} \mathrm{d}h\, p(h) + \tfrac{1}{24}p'(z-\tfrac{1}{2}) - \tfrac{7}{5760}p'''(z-\tfrac{1}{2}) + \ldots. \tag{41}$$

Introducing (38) and (13) we have

$$\rho(z) = \rho_g + (\rho_l - \rho_g)\left(\int_{\hat{z}}^{\infty} \mathrm{d}y\, \phi_0^2(y) + \frac{\gamma^2}{24}\frac{\mathrm{d}}{\mathrm{d}\hat{z}}\phi_0^2(\hat{z}) + \ldots\right) \tag{42}$$

with

$$\hat{z} = \gamma(z - \tfrac{1}{2}). \tag{43}$$

Explicit evaluation to order ε is straightforward and we obtain to first order

$$\rho(z) = \rho_g + (\rho_l - \rho_g)\{\tfrac{1}{2}\,\mathrm{erfc}(\hat{z}) + \varepsilon\pi^{-1/2}\exp(-\hat{z}^2)[(\tfrac{1}{48}\hat{z}^3 - \tfrac{5}{32}\hat{z})(2S^2+3) - \tfrac{1}{3}\hat{z}S^2]\} \tag{44}$$

with

$$\mathrm{erfc}(x) = 2\pi^{-1/2}\int_x^{\infty} \exp(-t^2)\,\mathrm{d}t.$$

The width W of the interface is essentially the inverse of the scaling factor γ,

$$W \simeq S^{-1/2} G^{-1/4}$$

diverging when the external field vanishes. The error function profile for a very weak field is in agreement with the capillary-wave model of Buff *et al* (1965).

Defining the width W more precisely through

$$W^2 = \sum_{h=-\infty}^{+\infty} h^2 p(h)$$

we find

$$W^2 = \gamma^{-2} \int_{-\infty}^{+\infty} \mathrm{d}y\, y^2[\phi_0(y)]^2 = (8\varepsilon S^2)^{-1}[1 - \tfrac{1}{4}(2S^2+3)\varepsilon + \mathcal{O}(\varepsilon^2)]$$

by means of (35). In terms of G,

$$W = \tfrac{1}{2} S^{-1/2} G^{-1/4}[1 - G^{1/2}(2S^2+3)/16S]. \tag{45}$$

The sign of the last term shows that the interface region is slightly narrower than the capillary-wave prediction.

From now on we prefer to work with the normalised density

$$\frac{\rho(z) - \rho_g}{\rho_l - \rho_g}$$

as our density. This is equivalent to the usual convention of $\rho_g = 0$ and $\rho_l = 1$ in lattice-gas models.

The gradient of this normalised density will be useful in § 8. From (44) we obtain

$$-\frac{\mathrm{d}\rho}{\mathrm{d}z} = \pi^{-1/2}\gamma \exp(-\hat{z}^2)[1 + \varepsilon(\tfrac{1}{24}\hat{z}^4 - \tfrac{3}{8}\hat{z}^2 + \tfrac{5}{32})(2S^2+3) + (\tfrac{1}{3} - \tfrac{2}{3}\hat{z}^2)S^2 + \mathcal{O}(\varepsilon^2)]. \tag{46}$$

5. Height correlations

The two-point height distribution function $p(h, h'; x)$ is the probability of simultaneously finding the heights $h_i = h$ and $h_{i+x} = h'$ of two columns separated by a distance x:

$$p(h, h'; x) = \langle \delta_{h_i,h} \delta_{h_{i+x},h'} \rangle.$$

Inserting the probability distribution (6) we obtain

$$p(h, h'; x) = Z^{-1}(T^x)_{hh'}(T^{L-x})_{h'h}. \tag{47}$$

Inserting the eigenfunction expansion (37) we find for $L \to \infty$

$$p(h, h'; x) = \sum_{n=0}^{\infty} (\lambda_n/\lambda_0)^x \psi_n(h)\psi_n(h')\psi_0(h)\psi_0(h'). \tag{48}$$

The first term in the sum represents the product of the independent height probabilities, and the remaining sum is, therefore, the height *correlation* function:

$$g(h, h'; x) = p(h, h'; x) - p(h)p(h') = \sum_{n=1}^{\infty} \exp(-x\kappa_n)\psi_n(h)\psi_n(h')\psi_0(h)\psi_0(h') \tag{49}$$

introducing $\kappa_n = \ln(\lambda_0/\lambda_n)$ from equation (36).

The corresponding density-density distribution function is

$$\rho(z, z'; x) = \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} p(h, h'; x) \tag{50}$$

and the density-density correlation function takes the form

$$H(z, z'; x) = \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} g(h, h'; x)$$

$$= \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} \sum_{n=1}^{\infty} \exp(-x\kappa_n)\psi_n(h)\psi_n(h')\psi_0(h)\psi_0(h'). \tag{51}$$

So far everything is exact. We now perform a weak-field expansion. To lowest order, i.e. with $\kappa_n = 2n\varepsilon$, equation (37) and $\psi_n(h) = \gamma^{1/2}\phi_n^{(0)}(y)$, the harmonic oscillator eigenfunctions, the sum in (48) takes the form

$$\sum_{n=0}^{\infty} \zeta^n \phi_n^{(0)}(y)\phi_n^{(0)}(y') = \pi^{-1}(1-\zeta^2)^{-1/2} \exp\left(\frac{-(1+\zeta^2)(y^2+y'^2)+4\zeta yy'}{2(1-\zeta^2)}\right)$$

of the harmonic oscillator propagator. Here

$$\zeta = \exp(-2\varepsilon x). \tag{52}$$

Taken together with the two remaining eigenfunctions in (46) we obtain the properly normalised two-point distribution function

$$p(y, y'; x) = \pi^{-1}(1-\zeta^2)^{-1/2} \exp\left(\frac{-y^2-y'^2+2yy'\zeta}{1-\zeta^2}\right). \tag{53}$$

Integrating out one variable, y' say, leads back to the square of the lowest-order eigenfunction, as it must by (38). The corresponding lowest-order correlation function is

$$g(y, y'; x) = \pi^{-1}(1-\zeta^2)^{-1/2} \exp\left(\frac{-y^2-y'^2+2yy'\zeta}{1-\zeta^2}\right) - \pi^{-1}\exp(-y^2-y'^2). \tag{54}$$

The distance along the interface, x, scales with ε. In other words, the interesting horizontal distance scale is when

$$\hat{x} = \varepsilon x \tag{55}$$

is of order unity.

It is clear from (52) that the horizontal correlation length is large, proportional to $1/\varepsilon$, and diverges in the weak-field limit (Reynardt 1983). For distances beyond this correlation length the correlations die off like

$$g(y, y'; x) \sim 2\pi^{-1} yy' \exp(-y^2-y'^2-2\varepsilon x). \tag{56}$$

As a different measure of the surface fluctuations we can use the mean square of height differences,

$$\Delta h(x) = \langle (h_i - h_{i+x})^2 \rangle = \sum_h \sum_{h'} (h-h')^2 p(h, h'; x). \tag{57}$$

Inserting the lowest-order result for $p(h, h'; x)$ we find

$$\Delta h(x) = \tfrac{1}{2} S^{-1} G^{-1/2}(1-e^{-2\varepsilon x}) \tag{58}$$

increasing linearly with distance when x is small compared with the horizontal correlation length. The $x \to \infty$ limit gives the width W of the interface

$$W = \langle h_i^2 \rangle^{1/2} = [\tfrac{1}{2}\Delta h(\infty)]^{1/2} = \tfrac{1}{2}S^{-1/2}G^{-1/4} \tag{59}$$

consistent with (45).

6. The density–density correlation function

The density-density correlation function $H(z, z'; x)$ is easily obtained from the height-height correlation function $g(h, h'; x)$:

$$H(z, z'; x) = \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} g(h, h'; x). \tag{60}$$

To lowest order, insertion of the height-height correlation function (54) gives, in the scaled variables (13) and (52),

$$H(y, y'; x) = \frac{1}{\pi} \int_y^\infty \mathrm{d}t \int_{y'}^\infty \mathrm{d}u \left[(1-\zeta^2)^{-1/2} \exp\left(\frac{-t^2 - u^2 + 2tu\zeta}{1-\zeta^2} \right) - \exp(-t^2 - u^2) \right]. \tag{61}$$

Differentiation of H with respect to ζ and use of the identity

$$\left(2\frac{\mathrm{d}}{\mathrm{d}\zeta} - \frac{\mathrm{d}^2}{\mathrm{d}t\,\mathrm{d}u} \right)(1-\zeta^2)^{-1/2} \exp\left(\frac{-t^2 - u^2 + 2tu\zeta}{1-\zeta^2} \right) = 0 \tag{62}$$

yields the more convenient representation

$$H(y, y'; x) = \frac{1}{2\pi} \int_0^\zeta \mathrm{d}v (1-v^2)^{-1/2} \exp\left(\frac{-y^2 - y'^2 + 2yy'v}{1-v^2} \right) \tag{63}$$

for the density-density correlation function. The correlations are clearly positive. Figure 1 shows that the correlation function is peaked at the surface. The large- and short-distance behaviour of (63) is easily obtained.

For large distances, i.e. $\hat{x} = \varepsilon x \gg 1$, $\zeta = \exp(-2\hat{x})$ will be small. Then (63) yields to first order in ζ:

$$H \simeq \frac{1}{2\pi} \exp(-y^2 - y'^2) \exp(-2\hat{x}) \qquad \hat{x} \gg 1. \tag{64}$$

Thus the horizontal correlation length is $1/2\varepsilon$.

For $x = 0$, on the other hand, $\zeta = 1$. The first term in the integrand in (61) simplifies when $\zeta \to 1$:

$$(1-\zeta^2)^{-1/2} \exp\left(-\frac{(t-u)^2}{1-\zeta^2} \right) \exp\left(\frac{-2ut}{1+\zeta} \right) \to \sqrt{\pi}\,\delta(t-u) \exp(-ut). \tag{65}$$

In terms of error functions this gives

$$H(y, y'; 0) = \tfrac{1}{2}\operatorname{erfc}(y_m) - \tfrac{1}{4}\operatorname{erfc}(y)\operatorname{erfc}(y') \tag{66}$$

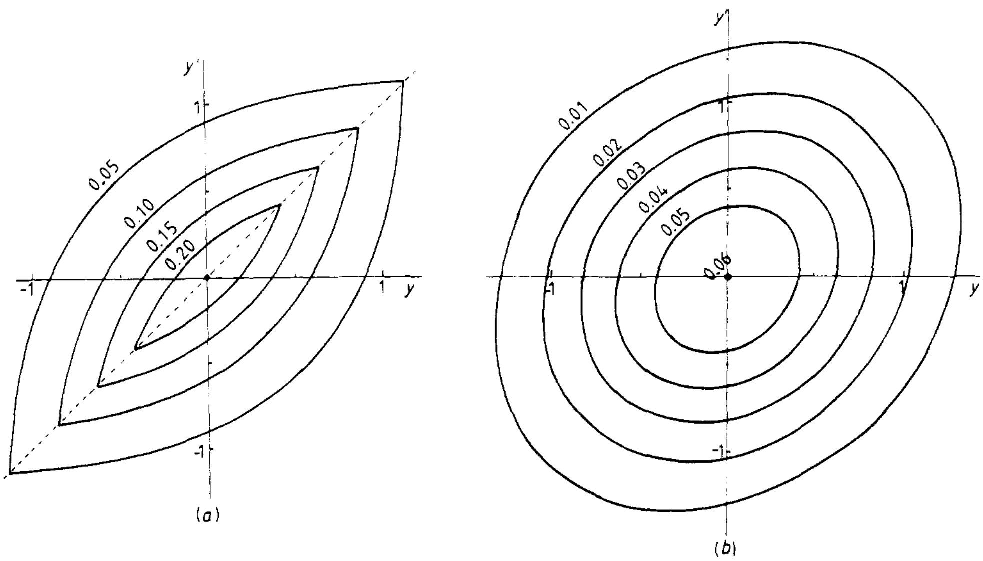

Figure 1. Contour lines for the density-density correlation function $H(y, y'; x)$ at (*a*) zero horizontal distance, $x = 0$, and (*b*) at a distance x equal to the horizontal correlation length, $x = 1/2\varepsilon$.

where $y_m = \max(y, y')$. Note that this is expressed in terms of the lowest-order density profile (44) as

$$H(y, y'; 0) = \rho(y_m) - \rho(y)\rho(y'). \tag{67}$$

This general relation follows from the definition of the density-density correlation function.

The correlation function has for $y = y'$ and short horizontal distances a ridge, which for $x = 0$ is non-analytic, with a discontinuity in slope across the ridge (figure 1(*a*)).

Naturally the correlation function decays with increasing horizontal distance. For large distances it is, by (64), always exponential. For the maximum value of H at $y = y' = 0$ one obtains easily from (63) the complete distance dependence:

$$H(0, 0; x) = \frac{1}{2\pi} \sin^{-1}(e^{-2\hat{x}}). \tag{68}$$

Stecki and Dudowicz (1986) tried to parametrise H, or rather the Fourier-transformed density-density correlation function

$$\tilde{H}(y, y'; k) = \sum_{x=-\infty}^{+\infty} \exp(ikx) H(y, y'; x) \tag{69}$$

in terms of the average and relative heights

$$Y = \tfrac{1}{2}(y + y') \qquad y_{12} = y - y' \tag{70}$$

as follows ($k = 0$ now):

$$\tilde{H}(Y, y_{12}) = \tilde{H}(0, 0) \exp(-\alpha y_{12}^2) \exp(-A_0 Y^2 - A_2 Y^4 - A_4 Y^6) \tag{71}$$

with

$$\tilde{H}(0,0) = SG^{-1/2}(H^* + H_1 G^{1/2} + \ldots) \tag{72}$$

$$\alpha = \alpha_0 + \alpha_1 (z - z')G^{1/2} + \ldots \tag{73}$$

$$A_n = A_{n0} + A_{n1}(z - z')G^{1/2} + \ldots \qquad n = 0, 2, 4. \tag{74}$$

Since our analytic results cannot be obtained in the form (71) we cannot check the numerical coefficients directly. However, as we will show, some comparisons of the lowest-order coefficients can nevertheless be made.

Stecki and Dudowicz give the value $H^* = 0.3465$ (for their choice of temperature $T = 0.3T_c$ or $K = 1.968\,956$). This we can compare since we can take $y = y' = 0$ and use (68):

$$H^* = S^{-1}G^{1/2}\int_{-\infty}^{+\infty} \mathrm{d}x\, H(0,0;x) = S^{-1}G^{1/2}\pi^{-1}\int_0^{+\infty} \mathrm{d}x \sin^{-1}(\mathrm{e}^{-2\varepsilon x}) \tag{75}$$

$$= \pi^{-1}\int_0^{+\infty} \mathrm{d}s \sin^{-1}(\mathrm{e}^{-s}) = \tfrac{1}{2}\ln 2$$

independent of K. The value $\frac{1}{2}\ln 2 = 0.346\,57\ldots$ checks perfectly with the numerical result just quoted.

Expansion around $y = y' = 0$ can give additional information. To lowest order (71) yields

$$\tilde{H}(k=0) = SG^{-1/2}H^*[1 - A_{00}Y^2 - \alpha_0 y_{12}^2 + (\tfrac{1}{2}A_{00} - A_{20})Y^4 + (A_{00}A_{20} - A_{40} - \tfrac{1}{6}A_{00}^3)Y^6 + \ldots]. \tag{76}$$

Expansion of the analytical result (63) and integration yields

$$\begin{aligned} H(y, y'; x) = H(0,0;x) + \pi^{-1}(1-\zeta^2)^{-1/2}\{ & Y^2[1 - \zeta - (1-\zeta^2)^{1/2}] \\ & - \tfrac{1}{4}y_{12}^2[1 + \zeta - (1-\zeta^2)^{1/2}] \\ & + \tfrac{1}{3}Y^4(1-\zeta^2)^{-1}[3\zeta - \zeta^3 - 2 + 2(1-\zeta^2)^{3/2}] \\ & - \tfrac{2}{45}Y^6(1-\zeta^2)^{-2}[7(1-\zeta^2)^{5/2} - (2\zeta^2 + 6\zeta + 7)(1-\zeta)^3] + \ldots\}. \end{aligned} \tag{77}$$

The term with y_{12}^2 diverges for $x \to 0$, reflecting the non-analyticity noted above. Integration over x now yields

$$\begin{aligned} \tilde{H}(k=0) = SG^{-1/2}\tfrac{1}{2}\ln 2\bigg[& 1 - \left(\frac{2}{\ln 2} - \frac{4}{\pi}\right)Y^2 - \left(\frac{1}{2\ln 2} + \frac{1}{\pi}\right)y_{12}^2 \\ & + \frac{2}{3\pi \ln 2}(4 + \pi - 4\ln 2)Y^4 + \frac{8}{45\pi\ln 2}(7\ln 2 - 11 - \pi)Y^6 \ldots \bigg]. \end{aligned} \tag{78}$$

Comparison between (76) and (78) determines the constants. The numerical values of this analytic computation are, with the Stecki–Dudowicz results in parentheses,

$$A_{00} = 1.612\,15 \quad (1.6121) \qquad \alpha_0 = 1.039\,657 \quad (\sim 1.0)$$

$$A_{20}/A_{00} = -0.0236 \quad (-0.0232)$$

$$A_{40}/A_{00} = -0.000\,798 \quad (-0.000\,93). \tag{79}$$

The small values of A_{20} and A_{40} indicate that $\tilde{H}$ is not far from Gaussian in the average height Y. In spite of the good agreement signalled in (79), there is, however, no theoretical basis for the parametrisation (71). It is therefore not surprising that Stecki and Dudowicz find it numerically unsatisfactory.

7. The direct correlation function

The direct correlation function $C(z_1, z_2; x)$ is the matrix inverse of H,

$$\sum_{x_2 z_2} H(z_1, z_2; x_1 - x_2) C(z_2, z_3; x_2 - x_3) = \delta_{z_1 z_3} \delta_{x_1 x_3} \tag{80}$$

or, alternatively,

$$\sum_{z_2} \tilde{H}(z_1, z_2; k) \tilde{C}(z_2, z_3; k) = \delta_{z_1 z_3}. \tag{81}$$

A discrete Fourier transform with respect to horizontal distance has been introduced:

$$\tilde{H}(z_1, z_2; k) = \sum_{x=-\infty}^{+\infty} e^{ikx} H(z_1, z_2; x). \tag{82}$$

In terms of eigenfunctions and eigenvalues of the transfer matrix we find readily from (49) that

$$\tilde{H}(z_1, z_2; k) = \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} \sum_{n=1}^{\infty} \psi_n(h) \psi_n(h') \psi_0(h) \psi_0(h') f_n(k) \tag{83}$$

with

$$f_n(k) = \frac{1 - e^{-2\kappa_n}}{1 + e^{-2\kappa_n} - 2\, e^{-\kappa_n} \cos k}. \tag{84}$$

Introducing the difference operator Δ_i through $\Delta_i F(\{z_n\}) = F(\{z_n\}) - F(\{z_n + \delta_{ni}\})$ we have by (51)

$$\Delta_1 \Delta_2 H(z_1, z_2; x) = g(z_1, z_2; x). \tag{85}$$

Proceeding formally, assuming that an inverse $\tilde{Q}$ to the height-height correlation function $\tilde{g}$ exists, i.e.

$$\sum_{z_2} \tilde{g}(z_1, z_2; k) \tilde{Q}(z_2, z_3; k) = \delta_{z_1 z_3} \tag{86}$$

we would have

$$\tilde{C}(z_1, z_2; k) = \Delta_1 \Delta_2 \tilde{Q}(z_1, z_2; k). \tag{87}$$

Finally, in terms of eigenfunctions and eigenvalues, the inverse to the height-height correlation function with the $n = 0$ included

$$\tilde{g}(z_1, z_2; k) = \sum_{n=0}^{\infty} \psi_n(z_1) \psi_n(z_2) \psi_0(z_1) \psi_0(z_2) f_n(k)$$

would be

$$\tilde{Q}(z_2, z_3; k) = \sum_{n=0}^{\infty} \psi_n(z_2) \psi_n(z_3) (\psi_0(z_2) \psi_0(z_3) f_n(k))^{-1} \tag{88}$$

as is seen by direct verification. Writing this as

$$\tilde{Q}(z_1, z_2; k) = \sum_{n=1}^{\infty} \psi_n(z_1) \psi_n(z_2) (\psi_0(z_1) \psi_0(z_2) f_n(k))^{-1} + f_0^{-1}$$

we obtain

$$\tilde{C}(z_1, z_2; k) = \Delta_1 \Delta_2 \sum_{n=1}^{\infty} \psi_n(z_1) \psi_n(z_2) (\psi_0(z_1) \psi_0(z_2) f_n(k))^{-1}. \tag{89}$$

Apparently we could include the $n=0$ term in $\tilde{g}$ since $f_0=0$ by (36). However, this means that the constant $1/f_0$ that is eliminated by the difference operators Δ_i is infinite. The basic difficulty with this formal derivation is that the inverse of g does not exist! The problem can be circumvented by using finite matrices with a cutoff M, i.e. $|z|\leq M$, introducing reduced matrices with one state (e.g. $z=-M$) excluded, and taking the limit $M\to\infty$ at the end (Stecki 1984). The result is (89).

From (89) we see that the k dependence of $\tilde{C}$ is very simple:

$$\tilde{C}(z_1, z_2; k) = C_0(z_1, z_2) + 2\cos(k) C_1(z_1, z_2). \tag{90}$$

This implies, as noted by Stecki (1984), that the direct correlation function is very short ranged:

$$C(z_1, z_2; x) = 0 \qquad \text{for } x > 1. \tag{91}$$

It remains to determine the weak-field form of the functions C_0 and C_1. We have in (89), since $\kappa_n = 2\varepsilon n + \mathcal{O}(\varepsilon^2)$

$$f_n^{-1} = \frac{1+\mathrm{e}^{-2\kappa_n} - 2\,\mathrm{e}^{-\kappa_n}\cos k}{1-\mathrm{e}^{-2\kappa_n}} \simeq (1-\cos k)/2n\varepsilon. \tag{92}$$

Replacing also $\psi_n(z)$ by $\gamma^{1/2}\phi_n^{(0)}(y)$ and Δ_i by $\gamma\,\mathrm{d}/\mathrm{d}y_i$ we have

$$\tilde{C} = \tfrac{1}{2}(1-\cos k)\gamma^2\varepsilon^{-1}\frac{\mathrm{d}}{\mathrm{d}y}\frac{\mathrm{d}}{\mathrm{d}y'}\sum_{n=1}^{\infty}\phi_n^{(0)}(y)\phi_n^{(0)}(y')(n\phi_0^{(0)}(y)\phi_0^{(0)}(y'))^{-1}. \tag{93}$$

Introducing the explicit harmonic oscillator functions

$$\phi_n^{(0)}(y) = (2^n n!)^{-1/2} H_n(y)\exp(-\tfrac{1}{2}y^2) \tag{94}$$

and using the property

$$\mathrm{d}H_n(y)/\mathrm{d}y = 2nH_{n-1}(y)$$

of the Hermite polynomials, we have

$$\begin{aligned}\tilde{C} &= (1-\cos k)\gamma^2\varepsilon^{-1}\sum_{n=1}^{\infty} H_{n-1}(y)H_{n-1}(y')[2^{n-1}(n-1)!]^{-1} \\ &= (1-\cos k)\gamma^2\varepsilon^{-1}\sqrt{\pi}\exp(\tfrac{1}{2}y^2+\tfrac{1}{2}y'^2)\delta(y-y')\end{aligned} \tag{95}$$

by completeness. Finally, by the definitions (16) and (17) of G and ε we obtain

$$C_0 = -2C_1 = 4S^2\sqrt{\pi}\exp(Y^2)\delta(y-y'). \tag{96}$$

Thus the direct correlation function varies rapidly with the height differences, but varies slowly with the average height Y. The range of rapid variation, in reality of $\mathcal{O}(1)$, has zero range on our length scale and appears as a δ function. A dependence

$$\tilde{C}_i(z, z') = \gamma^{-1} f_i(z, z')\exp(Y^2) \tag{97}$$

such that

$$\lim_{\gamma\to 0}\gamma^{-1} f_i(y/\gamma, y'/\gamma) \propto \delta(y-y') \tag{98}$$

would be consistent with the result (96).

Stecki and Dudowicz (1986) analyse their numerical results in terms of a parametrisation

$$\tilde{C}(z, z') = G^{-1/4}M(z-z')\exp(A_0Y^2 + A_2Y^4 + A_4Y^6) \tag{99}$$

similar to (97) since $\gamma \propto G^{1/4}$, equation (16). For $G \to 0$ they extrapolate numerically the coefficients $A_n(G)$ towards the values $A_0 \approx 1$, $A_2 \approx A_4 \approx 0$, in agreement with (97).

8. Susceptibilities

We have so far studied two-point correlation functions. A simpler quantity is the local susceptibility. This one-point function measures in our case the density response at a height z to a change in the external potential

$$\chi(z) = \frac{\delta\rho(z)}{\delta(-\beta V_{\mathrm{ext}})}$$

and is given by the susceptibility theorem (Stecki and Dudowicz 1986)

$$\chi(z_1) = \sum_{z'=-\infty}^{+\infty} \sum_{x'=-\infty}^{+\infty} H(z, z'; x-x') = \sum_{z'=-\infty}^{+\infty} \tilde{H}(z, z'; 0). \tag{100}$$

Insertion of expression (83) for the Fourier transform of the density-density correlation function yields

$$\chi(z) = \sum_{z'=-\infty}^{+\infty} \sum_{h=z}^{\infty} \sum_{h'=z'}^{\infty} \sum_{n=1}^{\infty} \psi_n(h)\psi_n(h')\psi_0(h)\psi_0(h') \frac{1+\mathrm{e}^{-\kappa_n}}{1-\mathrm{e}^{-\kappa_n}}. \tag{101}$$

We now perform the weak-field expansion. The expansion (37) of κ_n yields

$$\frac{1+\mathrm{e}^{-\kappa_n}}{1-\mathrm{e}^{-\kappa_n}} = \frac{1}{n\varepsilon} + \frac{n+1}{8n}(2S^2+3) + \mathcal{O}(\varepsilon). \tag{102}$$

The rather tedious evaluation of (101), relegated to appendix 2, gives the following result:

$$\chi = (S/2\pi)^{1/2} G^{-3/4} \exp(-\hat{z}^2)\{1 + G^{1/2}S^{-1}[(2S^2+3)(\tfrac{1}{48}\hat{z}^4 - \tfrac{3}{16}\hat{z}^2 + \tfrac{5}{64}) - \tfrac{1}{3}S^2\hat{z}^2 + \tfrac{1}{6}S^2]\} \tag{103}$$

with $\hat{z}$ defined in (43).

This may be compared with the parametrisation

$$\chi(z) = [(S/2\pi)^{1/2}G^{-3/4} + b_1 2^{-3/4} G^{-1/4} + \ldots] \exp[-(1 + a_1 G^{1/2} + \ldots)\hat{z}^2] \tag{104}$$

used by Stecki and Dudowicz (1986) to analyse their numerical results.

The constant and quadratic terms agree with (103) via the identification

$$a_1 = \tfrac{17}{24}S + \tfrac{9}{16}S^{-1} \tag{105}$$

$$b_1 = 2^{1/4}(\pi S)^{1/2}[\tfrac{5}{64}(2S^2+3) + \tfrac{1}{6}S^2]. \tag{106}$$

Numerically Stecki and Dudowicz, who worked at $K = 1.468\,956$, found $a_1 = 1.73$, $b_1 = 0.747\,912$. The analytic results (105) and (106) yield $a_1 = 1.730\,65$ and $b_1 = 0.748\,941$.

While the numerical agreement seems very satisfactory, the fact remains that the parametrisation (104) does not account for the fourth-order term in the exact expansion (103): the local susceptibility is *not* Gaussian beyond the lowest-order approximation.

We note in passing that the susceptibility (103) is, to the order computed, proportional to the negative gradient (46) of the density profile:

$$-\frac{\mathrm{d}\rho}{\mathrm{d}z} = \frac{mg}{kT}\chi(z).$$

This constitutes a check, through the two lowest orders in the low-gravity expansion, of the Wertheim identity

$$-\frac{d\rho}{dz}=\frac{mg}{kT}\int \tilde{H}(z, z'; k=0)\,dz'$$

derived for continuum fluids (Wertheim 1976).

By summing $\chi(z)$ over z Stecki and Dudowitz find the total susceptibility

$$\chi_T=\sum_z \chi(z)=2G^{-1}+wG^{-1/2}+\ldots \tag{107}$$

with $w=5.55\times10^{-5}$ for their value of K. Summing (integrating) our analytical expression (103) over z a remarkable cancellation occurs, and only one diverging term, namely

$$\chi_T=\tfrac{1}{2}G^{-1}=(mg\beta)^{-1} \tag{108}$$

remains. The numerical factor of G^{-1} in (107) is apparently a misprint in the reference. The smallness of the numerical coefficient w is consistent with our exact result $w=0$.

In a similar way a total susceptibility for $k\neq0$ may be defined

$$\tilde{\chi}_T(k)=\sum_{z=-\infty}^{+\infty}\sum_{z'=-\infty}^{+\infty}\tilde{H}(z, z'; k). \tag{109}$$

Since characteristic distances along the interface are of the order $1/\varepsilon$, the relevant k values are small:

$$k\equiv2\varepsilon\hat{k} \qquad \text{with } \hat{k}=\mathcal{O}(1). \tag{110}$$

In appendix 3 we show that

$$\tilde{\chi}_T(0)/\tilde{\chi}_T(\hat{k})=1+\hat{k}^2[1+(\tfrac{3}{4}S^{-1}+\tfrac{1}{2}S)G^{1/2}]+\mathcal{O}(G^{1/2}). \tag{111}$$

The dominating order agrees precisely with the capillary-wave theory prediction

$$\tilde{\chi}_T(0)/\tilde{\chi}_T(k)=1+(\beta\Gamma/2G)k^2=1+k^2L_c^2 \tag{112}$$

where Γ is the effective (angle-averaged) surface tension (Fisher *et al* 1982). Here

$$L_c=(\beta\Gamma/2G)^{1/2} \tag{113}$$

is the capillary length, the correlation length *along* the interface. To dominating order the value of the correlation length is $1/2\varepsilon$ in the present model, either from (64) or from (110) and (111).

Comparison between (111) and (112) yields to next order

$$\beta\Gamma=2S^2+(S^3+\tfrac{3}{2}S)G^{1/2}. \tag{114}$$

Stecki and Dudowicz find a similar parametrisation, with the numerical value 11.767 for the coefficient of the $G^{1/2}$ term (with $S=2.057\,27$). The analytic expression (114) gives the correct value 11.793.

9. Concluding remarks

We have in the present paper shown how to execute a weak-field asymptotic analysis of physical quantities for the present system, in particular the interface profile and the density-density correlation function. The dominating qualitative features of the model were already known through the numerical study of Stecki and Dudowicz (1986) that motivated the present work. However, the present approach clarifies the nature of the weak-gravity expansion, and we are able to obtain exact expressions for these physical quantities. The relation between our analytic approach and the numerical work has several aspects. The numerical work was mainly limited to one temperature, $T = 0.3\,T_c$, and what appeared as numbers in the numerical study is often in reality a function of temperature.

Moreover, we show that the functional form that was used to parametrise the numerical results are in some cases correct, in other cases incorrect.

To *dominating order* the results show Weeks' scaling (Weeks 1984): distances along the interface scale with the capillary length L_c, while distances normal to the interface scale with the interface width W. Both length scales diverge in the weak-gravity limit, since

$$W \propto g^{-1/4} \qquad L_c \propto g^{-1/2}. \tag{115}$$

The density variation shows, again to dominating order, the error-function profile

$$\rho(z) = \rho_g + \tfrac{1}{2}(\rho_l - \rho_g)\,\mathrm{erfc}(z/W) \tag{116}$$

of capillary-wave theory. (For a recent discussion of the reconciliation of the capillary-wave and the van der Waals theories of interfaces, see Höye (1987).)

The dominating-order density-density correlation function has, as already mentioned, the scaling form

$$H(z, z'; x) = H(z/W, z'/W; x/L_c) \tag{117}$$

which at large separations along the interface ($x \gg L_c$)—and *only* at large separations—is Gaussian in the vertical positions.

We also obtain corrections to scaling, of relative order $g^{1/2}$. An important feature of these contributions is that temperature now appears *explicitly*, not only through the length scales W and L_c. The correction increases the interface density gradient.

The direct density-density correlation function $C(z, z'; x)$ is exceptional in its scaling behaviour, or rather lack of such. As a function of the three variables average height $\frac{1}{2}(z+z')$, relative height $(z-z')$ and horizontal distance x it scales only in the former, the average height. Our present asymptotic expansion signals that the dependence on $(z-z')$ is short ranged, but does not resolve the fine structure of this dependence, seen in the numerical results of Stecki and Dudowicz. It remains to extract this behaviour analytically.

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Appendix 1. An Euler–Maclaurin formula

Purely formal operator manipulation on the Taylor expansion

$$p(h) = \exp[(h - z + \tfrac{1}{2})D]\,p(z - \tfrac{1}{2})$$

with $D = \mathrm{d}/\mathrm{d}z$, gives

$$\sum_{h=z}^{\infty} p(h) - \int_{z-1/2}^{\infty} \mathrm{d}h\, p(h) = \left(\frac{\mathrm{e}^{D/2}}{1-\mathrm{e}^{D}} + \frac{1}{D}\right) p(z-\tfrac{1}{2})$$

$$= [\tfrac{1}{24}D - \tfrac{7}{5760}D^3 + \mathcal{O}(D^5)]p(z-\tfrac{1}{2}) = \tfrac{1}{24}p'(z-\tfrac{1}{2}) - \tfrac{7}{5760}p'''(z-\tfrac{1}{2}) + \ldots .$$

More prudent derivations yield the same result.

Appendix 2. Weak-field expansion of the susceptibility

In this appendix we compute the local susceptibility to leading and next-to-leading order in the weak-field expansion. The starting point is (101):

$$\chi(z) = \sum_{n=1}^{\infty} \sum_{h=z}^{\infty} \sum_{z'=-\infty}^{+\infty} \sum_{h'=z'}^{\infty} \psi_n(h)\psi_0(h)\psi_n(h')\psi_0(h') f_n(k=0) \qquad \text{(A2.1)}$$

with

$$f_n(k=0) = \frac{1}{n\varepsilon} + \frac{n+1}{8n}(2S^2+3) + \mathcal{O}(\varepsilon). \qquad \text{(A2.2)}$$

We begin with the summation over z'

$$I_n = \sum_{z'=-\infty}^{+\infty} \sum_{h'=z'}^{\infty} \psi_n(h')\psi_0(h') = \sum_{h=-\infty}^{+\infty} h\psi_n(h)\psi_0(h)$$

with the last equality by partial summation. Inserting the expansion (22) for the eigenfunctions (13), we have to $\mathcal{O}(\varepsilon)$

$$\gamma I_n = \int_{-\infty}^{+\infty} \mathrm{d}y\, y\phi_n(y)\phi_0(y) = \int_{-\infty}^{+\infty} \mathrm{d}y\, y\phi_n^{(0)}(y)\phi_0^{(0)}(y)$$

$$+\varepsilon \int_{-\infty}^{+\infty} \mathrm{d}y\, y(\phi_n^{(1)}(y)\phi_0^{(0)}(y) + \phi_n^{(0)}(y)\phi_0^{(1)}(y)).$$

The first-order eigenfunction expression (30)

$$\phi_m^{(1)}(y) = \sum_k \alpha_{m,k}\phi_k^{(0)}(y) \qquad \text{(A2.3)}$$

with at most four non-zero coefficients, and the harmonic oscillator matrix elements

$$\int_{-\infty}^{+\infty} \mathrm{d}y\, y\phi_n^{(0)}(y)\phi_m^{(0)}(y) = \sqrt{m/2}\,\delta_{m,n+1} + \sqrt{n/2}\,\delta_{m,n-1} \qquad \text{(A2.4)}$$

gives

$$\gamma I_n = [1/\sqrt{2} - \tfrac{1}{16}\sqrt{2}(2S^2+3)\varepsilon]\delta_{n,1} + \tfrac{1}{16}\sqrt{3}(2S^2+3)\varepsilon\delta_{n,3} + \mathcal{O}(\varepsilon^2). \qquad \text{(A2.5)}$$

We have used the explicit expressions (31) for the expansion coefficients α. With the notation

$$J_n = \sum_{h=z}^{\infty} \psi_n(h)\psi_0(h) \qquad \text{(A2.6)}$$

we may write the susceptibility expression (A2.1) as

$$\chi(z)=\sum_{n=1}^{\infty} J_n I_n f_n(k=0)=J_1 I_1 f_1(k=0)+J_3 I_3 f_3(k=0). \tag{A2.7}$$

Since I_3 is already of order ε we need J_3 and f_3 to leading order only:

$$\gamma\varepsilon\chi(z)=J_1\sqrt{2}[\tfrac{1}{2}+\tfrac{1}{16}(2S^2+3)\varepsilon]+J_3\tfrac{1}{48}\sqrt{3}(2S^2+3)\varepsilon. \tag{A2.8}$$

Finally we must evaluate J_1 and J_3. The Euler-Maclaurin expression (41) yields

$$J_n=\sum_{h=z}^{\infty}\psi_n(h)\psi_0(h)=\int_{\hat{z}}^{\infty}\mathrm{d}y\,\phi_n(y)\phi_0(y)+\frac{\gamma^2}{24}\frac{\mathrm{d}}{\mathrm{d}\hat{z}}(\phi_n(\hat{z})\phi_0(\hat{z})) \tag{A2.9}$$

with $\hat{z}=\gamma(z-\frac{1}{2})$ as in (43). The last term is of $\mathcal{O}(\varepsilon)$ since $\gamma^2=4S^2\varepsilon$ by (16) and (17).

Insertion of the eigenfunction expansion (22) gives

$$J_n=\int_{\hat{z}}^{\infty}\mathrm{d}y\,\phi_n^{(0)}(y)\phi_0^{(0)}(y)+\varepsilon\int_{\hat{z}}^{\infty}\mathrm{d}y(\phi_n^{(1)}\phi_0^{(0)}+\phi_n^{(0)}\phi_0^{(1)})$$
$$+\tfrac{1}{6}S^2\varepsilon\frac{\mathrm{d}}{\mathrm{d}\hat{z}}(\phi_n^{(0)}(\hat{z})\phi_0^{(0)}(\hat{z})). \tag{A2.10}$$

It is clear that the following properties of the harmonic oscillator eigenfunctions:

$$\sqrt{2n}\,\phi_n^{(0)}(y)\phi_0^{(0)}(y)=-\frac{\mathrm{d}}{\mathrm{d}y}(\phi_{n-1}^{(0)}(y)\phi_0^{(0)}(y)) \tag{A2.11}$$

equivalent to the recursion

$$H_{n+1}(y)=2yH_n(y)-H'_{n-1}(y)$$

for Hermite polynomials, will enable us to execute the integrations in (A2.10). We find

$$J_3=6^{-1/2}\phi_2^{(0)}(\hat{z})\phi_0^{(0)}(\hat{z})+\mathcal{O}(\varepsilon)=(48\pi)^{-1/2}(4\hat{z}^2-2)\exp(-\hat{z}^2)+\mathcal{O}(\varepsilon) \tag{A2.12}$$

and, using

$$\phi_1^{(1)}=\alpha_{1,3}\phi_3^{(0)}+\alpha_{1,5}\phi_5^{(0)}$$

and

$$\phi_0^{(1)}=\alpha_{0,2}\phi_2^{(0)}+\alpha_{0,4}\phi_4^{(0)}$$

derived from (30) and (31), to first order in ε, we obtain

$$J_1=(2\pi)^{-1/2}\exp(-\hat{z}^2)[1+\tfrac{1}{24}\varepsilon(2S^2+3)(\tfrac{5}{4}-10\hat{z}^2+\hat{z}^4)-\tfrac{1}{3}\varepsilon S^2(2\hat{z}^2-1)]. \tag{A2.13}$$

Finally, insertion of (A2.12) and (A2.13) into (A2.8) gives

$$\chi(z)=(S/2\pi)^{1/2}G^{-3/4}\exp(-\hat{z}^2)+(2\pi S)^{-1/2}G^{-1/4}\exp(-\hat{z}^2)$$
$$\times[(2S^2+3)(\tfrac{5}{64}-\tfrac{3}{16}\hat{z}^2+\tfrac{1}{48}\hat{z}^4)+\tfrac{1}{6}S^2(1-2\hat{z}^2)]+\mathcal{O}(G^{1/4})$$

which is (103) in the main text.

Appendix 3. Evaluation of $\tilde{\chi}_{\mathrm{T}}(k)$

The k-dependent total susceptibility $\tilde{\chi}_{\mathrm{T}}$ can be obtained from the two-point density-density correlation function. By (83) and (109)

$$\tilde{\chi}_{\mathrm{T}}(k)=\sum_{n=1}^{\infty}\sum_{z=-\infty}^{\infty}\sum_{h=z}^{\infty}\sum_{z'=-\infty}^{\infty}\sum_{h'=z'}^{\infty}\psi_n(h)\psi_0(h)\psi_n(h')\psi_0(h')f_n(k). \tag{A3.1}$$

As in appendix 2 the summation over the heights can be done, with the result (A2.5). To $\mathcal{O}(\varepsilon)$ then

$$\gamma^2 \tilde{\chi}_{\mathrm{T}}(\hat{k}) = [\tfrac{1}{2} - \tfrac{1}{8}(2S^2+3)\varepsilon] f_1(\hat{k}) \tag{A3.2}$$

and thus

$$\frac{\tilde{\chi}_{\mathrm{T}}(0)}{\tilde{\chi}_{\mathrm{T}}(\hat{k})} = \frac{f_1(0)}{f_1(\hat{k})} = 1 + 2\,\mathrm{e}^{\kappa_1}(\mathrm{e}^{\kappa_1}-1)^{-2}[1-\cos(2\varepsilon\hat{k})]$$
$$= 1 + \sin^2(\varepsilon\hat{k})/\sinh^2(\kappa_1/2) = 1 + (2\varepsilon\hat{k}/\kappa_1)^2 + \mathcal{O}(\varepsilon^2).$$

Using the expansion (37) for κ_1 we find

$$\tilde{\chi}_{\mathrm{T}}(0)/\tilde{\chi}_{\mathrm{T}}(\hat{k}) = 1 + \hat{k}^2 + (\tfrac{3}{2} + S^2)\hat{k}^2\varepsilon + \mathcal{O}(\varepsilon^2). \tag{A3.3}$$

Expressing ε in terms of G, this is (111) in the text.

References

Bedeaux D 1986 *Adv. Chem. Phys.* 6447
Buff F B, Lovett R A and Stillinger F H 1965 *Phys. Rev. Lett.* **15** 621
Croxton C A 1980 *Statistical Mechanics of the Liquid Surface* (New York: Wiley)
Fisher M P A, Fisher D S and Weeks J D 1982 *Phys. Rev. Lett.* **48** 368
Höye J S 1987 *J. Stat. Phys.* **49** 297
Reynardt M 1983 *J. Stat. Phys.* **31** 679
Rowlinson J S and Widom B 1982 *Molecular Theory of Capillarity* (Oxford: Clarendon)
Stecki J, Ciach A and Dudowicz J 1986 *Phys. Rev. Lett* **56** 1482
Stecki J and Dudowicz J 1986 *J. Phys. A: Math. Gen.* **19** 775
van Leeuwen J M J and Hilhorst H J 1981 *Physica* **107A** 319
Weeks J D 1984 *Phys. Rev. Lett.* **52** 2160
Wertheim M S 1976 *J. Chem. Phys.* **65** 2377