Extended Capillary Waves and the Negative Rigidity Constant
in the d=2 SOS Model

by

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Abstract

The solid-on-solid (SOS) model of an interface separating two phases is exactly solvable in two dimensions (d=2) when the interface becomes a one-dimensional string. The exact solution in terms of the transfer matrix is recalled and the density-density correlation function \( H(z_1, z_2; \Delta x) \) together with its projections, is computed. It is demonstrated that the shape fluctuations follow the (extended) capillary-wave theory expression \( S(q) = kT/(D + \gamma q^2 + \kappa q^4) \) for sufficiently small wave vectors \( q \). We find \( \kappa \) negative, \( \kappa < 0 \). At \( q = 2\pi \) there is a strong nearest-neighbor peak. Both these results confirm the earlier findings as established in simulations in d=3 and in continuous space, but now in an exactly soluble lattice model.
I.**Introduction**

The shape fluctuations of interfaces are described by the capillary-wave theory\[1-10\]. Its principal result is that the Fourier spectrum of the fluctuations follows for small wave-vectors the $1/q^2$ divergence. The divergence may be damped by an external field or by finite size, as in the form $1/(D + \gamma q^2)$, valid in the limit $q \to 0$. Both $D$ and the interfacial tension $\gamma$ are positive. The scattering experiments scan an interval of wave vectors up to the nearest-neighbor peak and beyond and many authors have searched for an extension of the simple capillary-wave form. An obvious generalization appeared to be

$$S(q) = kT/(D + \gamma q^2 + \kappa q^4).$$

(1.1)

Sum rules require convergence of integrals over $q$ and $\kappa > 0$ seems natural. Additional input was provided by the fluctuations of other $(d-1)$–dimensional objects in $d$–dimensional systems, such as membranes and bilayers in liquid solvents. According to both theory and experiment, the fluctuations of those autonomous objects are ruled not by $\gamma$ but by rigidity coefficient coupled to the curvature. It seemed only natural to “improve” the theory of fluctuations of ordinary non-autonomous interfaces by incorporating a contribution of a hypothetical rigidity coefficient coupled to curvature. The latter contribution ought to be

$$kT/\kappa q^4$$

(1.2)

with $\kappa$ necessarily positive. The positivity condition is necessary for the free energy of the deformed state to be larger than the free energy of the undeformed state. In this way one arrives at the expression (1.1) with the expectation of all three constants being positive.

The first signs of inconsistency were signalled in a series of papers\[8\] where it was demonstrated that (for the long range attractive dispersion force, but not only) expression (1.1) is inadmissible and the last term must be replaced by $\kappa q^4 f(q)$ where the function $f$ contains nonanalytical terms with logarithms.

In a series of simulations by Molecular Dynamics of liquid-vapor surfaces, it was found independently\[6\] that all results pointed to a negative $\kappa$. A negative value disproved the interpretation of $\kappa$ as a rigidity coefficient. The unexpected results were
recently confirmed by simulations of capillary waves in other liquid systems[9]. In ei-
other case[6,9] the intermolecular attractions between particles, were technically of short
range because of the cutoffs.

It may be argued that these two independent simulation results[6,9] are also con-
firmed by scattering experiments; a negative $\kappa$ means that the denominator gets smaller
than it would have been without any $\kappa$, the scattering intensity gets bigger - and this was
observed for liquid-vapor surfaces[10]. Such an interpretation, however, is not generally
accepted and other, more complicated, explanations were sought[5,10].

It would be interesting to confirm or negate the finding of a negative $\kappa$ by a method
other than simulation, for example in a system or model which is soluble exactly.

II. The SOS model.

In the Solid-on-Solid (SOS) model in two dimensions $d=2$ [11-17], a microscopic
configuration of the interface is given by the collection of heights

$$\{h_i\}, \ i = 1, L; \ 1 \leq h_i \leq M$$ (2.1)

as illustrated in Fig.1. The strip is $M \times L$ and below we consider the limit $L \gg M$.
The other limit, $M \gg L$, has also been considered[14,17]. The ”vertical” variable is $h$
or $z$ at the horizontal position $x = a_0 j$, $0 < j \leq L$ and we take $a_0 = 1$. The ”height” is
limited to $0 \leq h \leq M$. The standard $d = 2$ SOS model[11,17] assumes the energy of a
given configuration as

$$E = \epsilon \sum |h_{i+1} - h_i|^n \quad \epsilon > 0$$ (2.2)

with $n = 1$. A Gaussian model ($n = 2$) can also be considered. Introducing the $M \times M$
transfer matrix

$$T(h, h') = Q^{|h-h'|}$$ (2.3)

with $Q \equiv \exp[-\epsilon/kT]$, we find that the partition function and correlation functions
can be expressed in terms of ordinary scalar products of matrices $T$. If the transfer
matrix is diagonalized - as it can be - all solutions are available, also as analytical
expressions[11][14][17][15]. There is a minor and unimportant approximation involved
in the analytical expressions for the eigenvectors and eigenvalues of the inverse of \( T^{-1} \) (see Appendix).

We have calculated the density-density correlation function \( \tilde{H}(z_1, z_2; q) \) and other quantities such as the density profile \( \rho(z) \) and the probability functions: one-point \( p(h) \) and two-point \( P(h_1, h_2; \Delta x) \) and \( \tilde{P}(h_1, h_2; q) \). The following relations take place

\[
p(h) = \rho(h + 1) - \rho(h); \quad p(h) = Z(h, 1)^2
\]  

(2.4)

where \( Z_1(h) = Z(h, 1) \) is the dominant eigenvector corresponding to the largest eigen-value \( \lambda_1 \). Moreover

\[
H = \sum_{h_1 \geq z_1} \sum_{h_2 \geq z_2} P(h_1, h_2) - p(h_1)p(h_2)
\]

(2.5)

at each value of \( \Delta x \equiv |x_2 - x_1| \). Calculation of the Fourier Transform gives

\[
\tilde{H}(z_1, z_2; q) = \sum_{h_1 \geq z_1} \sum_{h_2 \geq z_2} \sum_{j \geq 2} f_j(q) c_j(h_1)c_j(h_2),
\]

(2.6)

where

\[
c_j(h) = Z_j(h)Z_1(h).
\]

(2.7)

In

\[
f_j(q) = (1 - r^2)/(1 + r^2 - 2r \cos(q)),
\]

(2.8)

\( r \equiv r_j = \lambda_j/\lambda_1 < 1 \) and we never need \( j = 1 \). Periodic boundary conditions in the \( x \)–direction were assumed, \( h(x = 1) = h(x = L + 1) \); next the limit \( L \to \infty \) has been taken at constant \( M \). It is useful for the discussion of the \( q \)--dependence to introduce projections which result in functions of one variable, \( q \). One such function is \( \tilde{H}(q) \) which projects, at each \( q \), the matrix \( \tilde{H} \) onto \( p(h) \). A similar projection was used in \( d=3 \)[2,6].

\[
\tilde{H} = \sum_{h_1} \sum_{h_2} p(h_1)H(h_1, h_2)p(h_2).
\]

(2.9)

Since \( p(h) = Z_1(h)^2 \), by using (2.5) we can change the order of summations to make a computationally convenient expression.
Another projection is the height-height correlation function \( < h(x_1)h(x_2) > \) whose Fourier transform is the well known structure factor (of the interface)

\[
S(q) = < h_qh_{-q} > .
\] (2.10)

We have

\[
< h(x_1)h(x_2) > = \sum_h \sum_{h'} hh' [P(h,h';\Delta x) - p(h)p(h')]
\] (2.11)

and, constructing the Fourier sums,

\[
S(q) = \sum_h \sum_{h'} \sum_{j \geq 2} f_j(q) c_j(h)c_j(h')hh',
\] (2.12)

where the largest eigenvalue is excluded from the sum over the eigenvalue index \( j \). Alternatively the definition (2.6) of \( c_j \) can be invoked and the order of summation changed to give

\[
S(q) = \sum_{j \geq 2} f_j(q) d_j(q)^2
\] (2.13)

where

\[
d_j(q) \equiv \sum_h Z_j(h)hZ_1(h).
\] (2.14)

To summarize, we have so far the full density-density correlation function \( \tilde{H}(z_1,z_2,q) \), the corresponding \( z \)-derivative \( P(h_1,h_2,q) \) and the projections \( \tilde{H}(q) \) and \( S(q) \). Moreover, for a given value of \( q \), the density-density correlation function \( \tilde{H} \) is a \( M-1 \times M-1 \) positive definite matrix; it can be diagonalized and all its \( M-1 \) eigenvalues are functions of \( q \); the largest eigenvalue can be chosen and discussed as function of \( q \).

To make practical use of these expressions, the \( T \)-matrix is diagonalized as function of \( Q \) and this can be done analytically for small values of \( M \), or one can take the route through the inverse of \( T \), which is easier because the inverse is tridiagonal\[11\]. The final expressions are given in the appendix\[15\].

III. Results for the wave-vector dependence of correlations.

In order to reveal and illustrate the details of the capillary waves in the SOS model recalled and defined in the previous section, we numerically compute the analytical
expressions given in Section II and in the Appendix. In the Figures we show a selection of data, all for $Q = 0.5$.

The numerical computation of $\tilde{H}$, of the projection $\bar{H}$, and of the interfacial (string) structure factor $S(q)$, reveals three regions of the variable $q$. These regions are clearly visible in Fig.2. At the very lowest values of $q$ a plateau (in logarithmic scale) practically equal to the limit for $q = 0^+$ extends up to a crossover into the second and main region, that of the capillary waves. All the projections show a typical capillary-wave dependence of the form of (1.2), $1/\text{const} \cdot q^2$. This region extends up to $q^2 \sim 1 - 5$ where the amplitudes of the capillary waves have practically died out. Then in the third region ($q^2 > 5$) the nearest neighbour peak appears near $q \sim 2\pi$ i.e. in Fig.2 near $q^2 \sim 39$.

The plateau and the finite value at $q = 0^+$ are due to the finiteness of the width $M$ in the $z-$direction perpendicular to the interface. The excursions of the interface from the average position in the middle at $\sim M/2$ are damped like waves in a channel, of width $M$ and length $L$. This is captured by the smallest values of $q$.

The main capillary-wave region dominates in the middle region and is the main physical effect.

The wave-vector $q$ is measured in units of inverse lattice constant $a_0$, taken as unity here; hence the nearest neighbour peak expected at $2\pi/a_0$ occurs at $x = q^2 \sim 4\pi^2$. Its appearance was never considered in earlier work.

This simple fact is, however, of importance because the presence of the peak requires a raise in the structure factor at $q < 2\pi$, and this gradual raise takes place already at values of $q$ significantly lower than $2\pi$.

It may be found surprising that the raise begins so early.

The plots of $\tilde{H}$ for different sizes (widths) are shown in Fig.3. The plot of $S(q)$ in Fig.4 shows a curve common to all sizes in the central (capillary-wave) portion of the plot and the raise of $S(q)$ preceding the n.n. peak. Each of the $\tilde{H}(q)$ and $S(q)$ for each size $M$ were fitted to an empirical version of (1.1), i.e. to

$$S(x) = 1/(d + gx + K_4 x^2) \quad x \equiv q^2$$

where the constants $d, g, K_4$ or $g, K_4$ were estimated from the least-square fits. In all
cases but one the least-square fit produced a negative $K_4$. The same formula was used for fitting the largest eigenvalue of $\tilde{H}(z_1, z_2; q)$ and invariably negative $K_4$ was obtained. The raise in $S(q)$ can be mistakenly attributed to other reasons, if the existence of the faraway nearest-neighbour peak is neglected.

IV. Discussion

We have found in this exactly soluble lattice model in $d=2$ dimensions the same feature discovered earlier in two\cite{6,9} independent simulations: a raise in the structure factor over and above the capillary-wave contribution - which results in a negative value of the coefficient $\kappa$ in (1.1), to which the empirical coefficient $K_4$ is proportional. Therefore it cannot be interpreted as the rigidity of the interface.

There exist systems with capillary waves and positive $\kappa$: as mentioned in the introduction these are bilayers (and membranes) in $d=3$ immersed in a liquid solvent. For each such autonomous object there exists a surface area which minimizes the free energy. No such minimum exists in non-autonomous interfaces nor in the Ising or SOS model.

In general we must conclude that there exist several kinds of interfaces ruled by different laws. To strengthen this point one can invoke the existence of Langmuir monolayers with their numerous surface phases.

We may associate with the bilayers and membranes the term ”autonomous” and with ordinary liquid-vapor and liquid-liquid interfaces the term ”non-autonomous”.

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Appendix A.

The $T$-matrix given by (2.3) produces on inversion a tridiagonal matrix $\tau$ with diagonal elements given by

$$d = (1 + Q^2)/(1 - Q^2) \quad (A.1)$$

and all offdiagonal elements $\tau_{n,n+1}, \tau_{n,n-1}$ given by

$$o = -Q/(1 - Q^2) \quad (A.2)$$

Strictly speaking not all diagonal elements are equal to $d$; the first and the last element are

$$\tau_{11} = \tau_{MM} = d_0 = 1/(1 - Q^2) \quad (A.3)$$

For large $M$, safely $d$ can be substituted for $d_0$ and the resulting matrix $\tau'$ has the following eigenvalues[15]

$$\Lambda_j = (1 + Q^2 - 2Q \cos(b_0 j))/(1 - Q^2) \quad (A.4)$$

where $b_0 = \pi/(N + 1)$ and $j = 1, \cdots, M$. Hence $j=1$ corresponds to the smallest eigenvalue, i.e. to the largest eigenvalue of the original matrix $T$, equal to $1/\Lambda_1$. The eigenvectors are

$$Z_j(h) = (1/N) \cos(b_0 j \nu) \quad (A.5)$$

for $j$ odd, and

$$Z_j(h) = (1/N) \sin(b_0 j \nu) \quad (A.6)$$

for $j$ even. These eigenvectors are orthonormal and complete. The dimensions of the matrices are $M \times M$ and $M$ is best taken odd. The norm is $N^2 = (M + 1)/2$ and $\nu = h - 1 - (M + 1)/2$ so that $\nu = -(M + 1)/2, \cdots, 0, \cdots, +(M + 1)/2$.

The eigenvectors are common to the diagonalized matrix and its inverse whereas the eigenvalues are the inverses. Because $T$ is a symmetric positive definite matrix, it admits a representation

$$T_{h_1, h_2} = \sum_j Z_j(h_1)(1/\Lambda_j)Z_j(h_2) \quad (A.7)$$

and this representation for $T$ was used to obtain expressions in Section II, remembering that (A.4) refers to the inverse of $T$. 

8
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Figure Captions.

Caption to Fig.1

A portion of the SOS interface (which must be without overhangs or clusters). The lattice constant is 1, ordinates are \( x = j \) and abscissae are \( h(x) = h_j \leq M \).

Caption to Fig.2

An example of the projection \( \bar{H}(q) \) plotted against \( x \equiv q^2 \) in a range wide enough to display all three regions; the plateau, the main capillary wave region \( \bar{H} \sim 1/x \); and the nearest neighbour peak at \( x \sim 4\pi^2 \). This particular curve for \( M = 31 \) was fitted to Eq.(3.1) with \( d = 0.2964, g = 122.40, K_4 = -8.0. Q = 0.5 \).

Caption to Fig.3

The projections \( \bar{H}(q) \) plotted against \( x \equiv q^2 \) for the following widths \( M \) of the strip \( M= 120,001; 12001; 1201; 601; 301; 121; 61; - \) from lowest values to the highest in that order. The line is \( y = 1.e - 6/x \) to which all \( \bar{H} \) are parallel, perfectly so in the center of the plot. All curves were fitted to eq.(1.1) and all fits produced negative \( K_4 \). \( Q = 0.5 \).

Caption to Fig.4

The interfacial structure factor \( S(x) \) defined by (2.10) plotted against \( x \equiv q^2 \) for the widths \( M= 120001(crosses), 12001(plus signs), 1201(stars), 121(boxes), \) and the line fitted to (1.1). The nearest-neighbor peak and the faint increase in \( S \) for \( q > 0.1 \) are to be noticed. This faint increase forces a negative \( \kappa \). \( Q = 0.1 \). The slope is practically equal to the stiffness coefficient[17], which explicitly is \( (1 - Q^2)/(2Q) \).
