A STATISTICAL FIELD THEORY APPROACH APPLIED TO THE LIQUID VAPOR INTERFACE

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In recent years there has been a renewed interest in the utilization of statistical field theory methods for the description of systems at equilibrium both in the vicinity and away from critical points, in particular in the field of liquid state physics. These works deal in general with homogeneous systems, although recently the study of liquids in the vicinity of hard walls has also been considered in this way. On the other hand, effective Hamiltonian pertaining to the ϕ^4 theory family have been written and extensively used for the description of inhomogeneous systems either at the simple interface between equilibrium phases or for the description of wetting. In the present work, we focus on a field theoretical description of the liquid vapor interface of simple fluids. We start from the representation of the grand partition function obtained from the Hubbard–Stratonovich transform leading to an exact formulation of the problem, namely neither introducing an effective Hamiltonian nor associating the field to the one-body density of the liquid. Using as a reference system the hard sphere fluid and imposing the coexistence condition, the expansion of the Hamiltonian obtained yields a usual ϕ^4 theory without an unknown parameter. An important point is that the so-called capillary wave theory appears as an approximation of the one-loop theory in the functional expansion of the Hamiltonian, without any need to an underlying phenomenology.

Key words: field theory, gas-liquid interface, surface tension.

I. INTRODUCTION

The structure in the interface between two fluid phases at coexistence plays a central role in numerous specific situations, as for instance wetting transitions and related phenomena [1–7], and presents a great interest in itself from a theoretical point of view. Interfaces between coexisting subcritical phases at equilibrium provides some of the key features of more complex situations. For simple fluids the most important characteristic is the presence of thermally activated capillary waves [8] and their coupling with bulk fluctuations. Capillary waves are usualy described through the introduction of an effective surface Hamiltonian written as a functional of the interface height $h(\mathbf{s})$ ($\mathbf{s}$: coordinate parallel to the interface) and *a priori* built from a phenomenological description of the interface. Then this Hamiltonian, $H[h(\mathbf{s})]$, can be treated in the framework of field theoretical methods [2, 4], or renormalization group (RG) [9] theory. Recently, the hierarchical reference theory (HRT) has been generalized for the inhomogeneous case in order to deal with wetting transitions [7].

At the liquid vapor interface when $H[h(\mathbf{s})]$ is treated at the Gaussian level the capillary wave theory (CWT) is recovered, leading to the well known $1/q^2$ behavior for the height-height structure factor $S_{\Delta z \, \Delta z}(q)$. Using a 3D ϕ^4 model [5, 6, 10, 11] the theory has been extended in the sense that the stochastic variable of the effective

Hamiltonian does not coincide any more with the height $h(\mathbf{s})$. An alternative way to deduce an effective Hamiltonian from a DFT functional including the effect of the local curvature of the interface has been introduced in refs. [12, 13]. Recently [14], a model for the density profile based on an extension of a displaced profile type of approximation, where the profile is written as a function of $(z - h(\mathbf{s}))$ was considered. In addition, together with the surface fluctuations described by the height $h(\mathbf{s})$, the bulk phase fluctuations are added.

The purpose of the present work is to provide a simple description of the liquid / vapor interface structure of simple fluids in the framework of statistical field theory. We start from the Hubbard Stratonovich (KSSHE) [15] transform to get a representation of the grand-potential from which we deduce the surface tension and the surface structure factor at the the so-called one loop approximation level. This is done *via* the determination of the eigenvalues and eigenfunctions of the second functional derivative of the mean field KSSHE Hamiltonian. Taking into account the whole spectrum of eigenstates is of outmost importance for obtaining the correct result. One of the salient points of this work is that one recovers both the CWT and its first extension, namely the appearance of the bending rigidity factor k and the coupling between surface and bulk correlations in $S(q)$, without invoking any *ad hoc* phenomenology.

II. KSSHE TRANSFORM AND MEAN-FIELD APPROXIMATION

We briefly recall the important steps leading to the approriate statistical field theory formulation of the problem; the interested reader is refered to ref. [15,16] and [17] for an alternative formulation. We consider a simple fluid whose pair interaction potential includes a hard sphere repulsive part and a soft attractive part, denoted v(r). Let $w(r) = -\beta v(r)$ as usual and suppose that only purely attractive potentials are considered (w is a positive definite operator, $i.e.$ $\tilde{w}(k) > 0$). In the core region ($r < \sigma$), w can be chosen at will or regularized in order to fulfill a conveniently chosen criterion. We work in the grand canonical ensemble, namely at the constant chemical potential $\nu = \beta\mu$, and we consider the GC partition function related to the grand potential $\Xi = \exp(-\beta\Omega)$. Using the Hubbard Stratonovich transformation one can get Ξ in the form of a functional integral of $\exp(-H[\phi])$ over the field $\phi(\mathbf{r})$ which makes the link with statistical field theory, $H[\phi]$ being the effective Hamiltonian

$$H = \frac{1}{2}\langle\phi|w^{-1}|\phi\rangle - \ln(\Xi_{\mathrm{HS}}[\bar{\nu} + \phi]), \qquad (1)$$

with $\bar{\nu} = \nu - w(0)/2$ and $\Xi_{\mathrm{HS}}[\nu]$ is the hard sphere grand partition function at the local chemical potential $\nu(\mathbf{r})$. A Landau–Ginzburg form is obtained from a functional Taylor expansion of $\ln(\Xi_{\mathrm{HS}})$ arround some reference chemical potential of the hard sphere fluid, ν_0. Performing an expansion up to order k^2 of the propagator, $\tilde{\Delta}^{-1}(k) = K_0 + K_2 k^2$, we are left with

$$H[\phi] = H_0 + \int \left(\frac{K_2}{2}\left(\frac{\partial\phi}{\partial\mathbf{r}}\right)^2 \right.$$
$$\left. + \frac{K_0}{2}\phi^2 + V(\phi) - B\phi \right)d\mathbf{r} \qquad (2a)$$

$$V(\phi) = \sum_{n\geq 3}\frac{u_n}{n!}\phi^n \qquad (2b)$$

$$u_n = -\frac{\partial^n(\beta P_{\mathrm{hs}})}{\partial\nu^n}(\nu = \nu_0) \equiv -(\beta P_{\mathrm{hs}})^{(n)}[\nu_0] \qquad (2c)$$

where in addition, we have neglected the k^2 dependence of the u_n and made the translation $\phi \to \phi + \bar{\nu} - \nu_0$, ν_0 arbitrary. This formulation allows an exact mapping between the densities and their correlations with the mean value and the correlations of the field [15]. For instance, at the coexistence, the densities ρ_l and ρ_g of the two phases correspond to the two values $\langle\phi\rangle_l$ and $\langle\phi\rangle_g$. The external field B in (2a) is given by:

$$B = w^{-1} * \Delta\nu + \rho_{\mathrm{hs}}[\nu_0] \quad \text{with} \quad \Delta\nu = \bar{\nu} - \nu_0.$$

The value of ν_0 can be chosen in such a way that the ϕ^3 term vanishes and the coexistence condition between the liquid and vapor phases is $B = 0$. K_0 is

related to the deviation from the critical temperature: $t = (T_c - T)/T_c \propto (-K_0)$. The interaction part of the Hamiltonian is denoted by $V(\phi)$.

In the inhomogeneous system, we assume a special realization of the two phases coexistence: we impose explicitly the occurence of a bulk liquid and a bulk gas, at densities ρ_l and ρ_g separated by a planar surface located at $z = z_0$. The inhomogeneous mean field equation, $\delta H[\phi]/\delta\phi(z) = 0$, leads to the mean field profile $\phi_c(z) = \phi_b \tanh(c(z - z_0))$, when $V(\phi)$ is restricted to the order ϕ^4. Here, $c = (-K_0/2K_2)^{1/2}$, the inverse of the bulk correlation length, is also the inverse of the intrinsic interface width and $\to 0$ as $t^{1/2}$ when $t \to 0$. The mean field surface tension follows from the identity $\Omega_{\mathrm{MF}}[\nu] = H[\phi_c(z)]$ with the result

$$\beta\sigma^2\gamma_{\mathrm{MF}} = 4\sigma^2(-2K_2K_0^3/u_4^2)^{1/2},$$

which is similar to the expression given by Brilliantov [11] althought with however another definition for the reference system. Note that for $t \to 0$, $\gamma_{\mathrm{MF}} \sim t^{3/2}$. Finaly, for numerical calculations, we took for the u_n their Carnahan Starling values and the potential is regularized either in a W.C.A. scheme or from ref. [22].

III. ONE LOOP EQUATIONS

In order to go beyond the mean-field level we expand the Hamiltonian in the vicinity of $\phi_c(z)$. The first correction stems from the second order term and we have ($z_0 = 0$),

$$H[\phi = \phi_c + \chi] \simeq H[\phi_c]$$
$$+ \frac{1}{2}\int \chi(1)H^{(2)}(1,2)\chi(2)d1d2 \qquad (3)$$

Introducing the function $g(z) = (K_0 + V''(\phi_c(z)))/K2$, after a Fourier transform parallel to the surface, the operator $H^{(2)}$ is diagonalized in the set of the eigenfunctions φ_n solution of the eigenvalues equation ($\varepsilon_n = K_2(q^2 + c^2\omega_n)$)

$$K_2\left(-\frac{\partial^2}{\partial z^2} + q^2 + g(z)\right)\varphi_n(z) = \varepsilon_\omega\varphi_n(z) \qquad (4)$$

the solutions of which are known [5, 18]; the spectrum of eigenfunctions includes two bound states, $\varphi_0 = C_0/\cosh^2(cz)$ and $\varphi_1 = C_1\sinh(cz)/\cosh^2(cz)$, with $\omega_0 = 0$, $\omega_1 = 3$, respectively and a subset of unbounded states, or continuum spectrum $\varphi_k(z)$, with $k = c\sqrt{\omega_k - 4}$ which behave as plane waves in the bulk phases, $i.e.$ far from the interface, and are given by

$$\varphi_k(z) = C_1(k)e^{ikz}$$
$$\times\left[2 - \frac{k^2}{c^2} - \frac{3i}{c}k\tanh(cz) + 3(\tanh^2(cz) - 1)\right] \qquad (5)$$

It is important to note that $\varphi_0(z) \propto \partial\phi_c(z)/\partial z$. Then the subset of unbounded eigenstates must be orthogonalized; using the eigenvalue equation (4) and given the form of

$\varphi_k(z)$ (5), we get a non-trivial dispersion relation leading to the density of states ($x = k/c$)

$$\rho(k) = \frac{L}{\pi} - \frac{1}{\pi c}\left[\frac{1}{(1+x^2)} + \frac{2}{(4+x^2)}\right] = \frac{L}{\pi} + \frac{f(x)}{c} \quad (6)$$

where L is the size of the system in the z direction. It is important to note that $\int_{-\infty}^{\infty} f(x)dx = -2$ which proved useful in all calculations. Zittartz [18] have already got this density of states but without explicitly mentionning the need of orthogonalization. In [19] a similar kind of dispersion relation was obtained in the modelling of the charge density profile of electrolytes in the framework of another field theory. We emphasize that the orthogonalization of the eigenstates is of crucial importance for the calculation of Gaussian functional integrals. In order to calculate $\ln(\Xi)$ and the correlation functions, we write the fields $\chi(\mathbf{r})$ in the basis which diagonalizes the operator $H^{(2)}$, namely a Fourier transform in the direction $\mathbf{s}$ and a projection on $\varphi_\lambda(z)$ where $\{\lambda\} = \{n = 0, 1; k\}$ denotes the whole spectrum of eigenstates. From usual Gaussian functional integrals [20] we get

$$\ln(\Xi) = -H[\phi_c] + \frac{V}{2}\int \frac{d\mathbf{k}}{(2\pi)^3}\ln\left(\frac{\hat{w}^{-1}(k)}{\varepsilon_k(q)}\right) \quad (7)$$

$$-\frac{S}{2}\int \frac{d\mathbf{q}}{(2\pi)^2}\left(\sum_n \ln(\varepsilon_n(q)) + \int dk f(k/c)\ln(\varepsilon_k(q))\right)$$

where ε_k corresponds to the second functional derivative of the Hamiltonian for the ϕ^4 homogeneous model taken at $\phi = \phi_c(\pm L)$. Therefore, the volume term of $\ln(\Xi)$ in (7) is nothing but βpV at the one loop level of approximation [15]. We finally write the surface term of $\ln(\Xi)$ in terms of the surface tension $\gamma = [\ln(\Xi_b) - \ln(\Xi)]/S = \gamma_{\mathrm{MF}} + \gamma^{(1)}$. We obtain ($\gamma^{(1*)} = \beta\gamma^{(1)}\sigma^2$)

$$\gamma^{(1*)} = \frac{1}{8\pi}\left[(x - c^2)\ln\left(1 - \frac{2c}{\sqrt{x}+c}\right)\right.$$
$$\left.+ (x - 4c^2)\ln\left(1 - \frac{4c}{\sqrt{x}+2c}\right) - 6c\sqrt{x}\right]_{q_m^2+4c^2}^{q_M^2+4c^2} \quad (8)$$

where q_m and q_M are the lower and upper bound, respectively, of the integral over q. A similar result was obtained in [18] for a spin model. This result differs from that obtained in [4] where only the $n = 0$ eigenstate is kept.

We now consider the calculation of the field two-body correlation functions, $G(1,2) = \langle\chi(1)\chi(2)\rangle_H$. More precisely, we focus on the Fourier transform parallel to the surface, $G(z_1, z_2, q)$. For this we have to calculate the sum

$$\sum_\lambda \frac{\varphi_\lambda(z_1)\varphi_\lambda^*(z_2)}{\varepsilon_\lambda(q)}$$
$$= \sum_{n=0,1} \frac{\varphi_n(z_1)\varphi_n(z_2)}{\varepsilon_n(q)} + \int \rho(k)\frac{\varphi_k(z_1)\varphi_k^*(z_2)}{\varepsilon_k(q)}\,dk$$

A contribution of the integral over k cancels exactly the direct contribution of the two bound states, which shows,

once again, that the approximation consisting in keeping only the $\varphi_0(z)$ eigenmode is not sufficient. The result is ($z_\rangle, z_\langle = \sup, \inf(z_1, z_2)$)

$$G(z_1, z_2, q) = \frac{9}{2cK_2}\frac{\exp\left(-c|z_{12}|\left(\left(\frac{q}{c}\right)^2 + 4\right)^{1/2}\right)}{\left(\left(\frac{q}{c}\right)^2 + 4\right)^{1/2}\left(\frac{q}{c}\right)^2\left(\left(\frac{q}{c}\right)^2 + 3\right)}$$
$$\times\left[1 + \frac{q^2}{3c^2} + \left(\left(\frac{q}{c}\right)^2 + 4\right)^{1/2}\tanh(cz_\rangle) + \tanh^2(cz_\rangle)\right]$$
$$\times\left[1 + \frac{q^2}{3c^2} - \left(\left(\frac{q}{c}\right)^2 + 4\right)^{1/2}\tanh(cz_\langle) + \tanh^2(cz_\langle)\right] \quad (9)$$

IV. RESULTS AND DISCUSSION

Capillary behavior and surface structure factor

We started from the expansion of the effective Hamiltonian on the basis of the eigenstates $\varphi_\lambda(z)$. The first eigenstate, $\varphi_0(z)$ is proportional to the derivative of the mean field result $\phi_c(z)$, the proportionality constant being determined by the normalization. If we keep only this first eigenstate, the expansion of χ reads $\chi(\mathbf{s}, z) = \xi(\mathbf{s})\varphi_0(z)$. Hence the field takes the form $\phi(z) = \phi_c(z - z_{\mathrm{int}}(\mathbf{s}))$ and only the linear term in the expansion of ϕ with respect to z_{int} is kept. This corresponds to the so-called rigidly displaced profile approximation, where $z_{\mathrm{int}} = -a\xi(\mathbf{s})$ represents the fluctuating location of the interface. The corresponding contribution to H is a functional of $\xi(\mathbf{s})$ which defines an effective surface Hamiltonian given by

$$H_s^{(0)}[\xi(\mathbf{s})] = \frac{1}{2}\int d\mathbf{s}\left[K_2(\partial_\mathbf{s}(\xi(\mathbf{s}))^2 + \omega_0\xi(\mathbf{s})^2\right] \quad (10)$$

using $\omega_0 = 0$, and the mean field equation yielding $K_2/a^2 = \beta\gamma_{\mathrm{MF}}$ we rewrite (10) in the form

$$H_s^{(0)} = \frac{1}{2}\beta\gamma_{\mathrm{MF}}\int d\mathbf{s}(\partial_\mathbf{s}(z_{\mathrm{int}}(\mathbf{s}))^2 = H_{\mathrm{CWT}} \quad (11)$$

which coincides with the usual effective surface Hamiltonian of the CWT theory for the free surface, *i.e.* in the absence of external field. Therefore we obtain the CWT as the lowest approximation beyond the mean field approximation without invoking phenomenological arguments.

The structure is also characterized by the height-height correlation function, $\langle z_{\mathrm{int}}(\mathbf{s}_1)z_{\mathrm{int}}(\mathbf{s}_2)\rangle$ or its Fourier transform parallel to the surface which defines the surface structure factor, $S_{\Delta z \Delta z}(q)$, where $z_{\mathrm{int}}(\mathbf{s})$ is the location of the interface relative to its mean value. We consider $\int \chi(\mathbf{s}, z)dz/\Delta\phi_b$, where $\Delta\phi_b = \phi_c(L) - \phi_c(-L)$, as a measure of the instantaneous location of the surface at $\mathbf{s}$, which amounts to define the location of the surface from a constraint on the integral of χ, as is done

in [14] for the density profile. We are then led to identify $S_{\Delta z \, \Delta z}(q) = (\Delta\phi_c(b))^{-2} \int G(z_1, z_2, q)dz_1 dz_2$, which corresponds to the S_{ic} used in [14]. It is important to notice that the coupling with the bulk fluctuations are included in the present formulation through the eigenstates of the continuum. We also introduce the effective surface width, or surface corrugation, $\sigma^{\text{eff}} = \sqrt{\langle z_{\text{int}}(\mathbf{s}_1) z_{\text{int}}(\mathbf{s}_1)\rangle}$.

The behavior of $S_{\Delta z \, \Delta z}(q)$ is analysed from the function $\tilde{g}(q) = \int dz_1 \int dz_2 G(z_1, z_2, q)$. From (9) we get for the leading term of $G(z_1, z_2, q)$ when $q \to 0$

$$G(z_1, z_2, q \to 0) \simeq \frac{1}{K_2 q^2}\varphi_0(z_1)\varphi_0(z_2) \qquad (12)$$

which corresponds to the CWT behavior. Then it is easy to show that $1/(\Delta\phi_b)^2\tilde{g}(q \to 0) \to 1/(\gamma_{\text{MF}}q^2)$ from the relation already used between the normalization of $\varphi_0(z)$ and γ_{MF} $((\int \varphi_0(z)dz)^2 = (\Delta\phi_b)^2 K_2/\gamma_{\text{MF}})$. This is exactly the CWT behavior, leading to the well known logarithmic divergence of the surface corrugation for which we get $(\sigma^{\text{eff}})^2 = (4\pi\gamma_{\text{MF}})^{-1}\ln(q_M^2/q_m^2)$.

It can be shown from (9) that the contribution to $\tilde{g}(q)$ diverging with the system size, due to the bulk correlations, is exactly $(2L)$ times the integral of $G_b(z_{12}, q)$, the correlation function of the bulk phase, over z_{12} If we keep only these two terms we get

$$S_{\Delta z \, \Delta z}(q) \simeq \frac{2L}{\Delta\Phi^2}\int G_b(q, z_{12})dz_{12} + \frac{1}{\gamma_{\text{MF}}q^2} \qquad (13)$$

Given that the bulk term vanishes when $q \to 0$, we see that (13) presents a cross-over like behavior in terms of wave vector q, where a threshold value q_s naturally appears, separating the capillary wave behavior at small values of q from the bulk like behavior at $q > q_s$, with q_s given by

$$q_s \sim \left[\left(2L\gamma_{\text{MF}}/\Delta\Phi^2 \right) \int G_b(q, z_{12})dz_{12} \right]^{-1/2}.$$

Such a behavior is in agreement with that of Refs. [14,21]; however, in the present formulation the bulk fluctuations come out of the calculation through the continuum subset of eigenstates and have not to be added to the field profile. Furthermore, from (13) we can drop exactly the bulk contribution, and doing this we define a purely interfacial contribution to $S_{\Delta z \, \Delta z}(q)$ (see Fig. 1).

$$S_{\text{int}}(q) = S_{\Delta z \, \Delta z}(q) - (2L/\Delta\phi_b^2)\int G_b(q, z_{12})dz_{12} \quad (14)$$

Then the departure of $S_{\text{int}}(q)$ from its $1/q^2$ behavior allows us to isolate the deviations from the capillary wave like behavior of $S_{\Delta z \, \Delta z}(q)$. To this aim we define $\beta(q) = (q^2 S_{\text{int}}(q))^{-1} - \gamma_{\text{MF}}$. $\beta(q)/q^2$ is found nearly constant and thus leads us to define a bending rigidity of the interface,

$$\kappa = \lim_{q \to 0}((1/q^2)\beta(q)) \simeq ((1/q^2)\beta(q)) \qquad (15)$$

which takes a positive value, as it should be for the stability of the interface [13]. In other words, the small q behavior of $S_{\text{int}}(q)$ is

$$S_{\text{int}}(q) \simeq 1/[\gamma_{\text{MF}}q^2 + \kappa q^4]$$

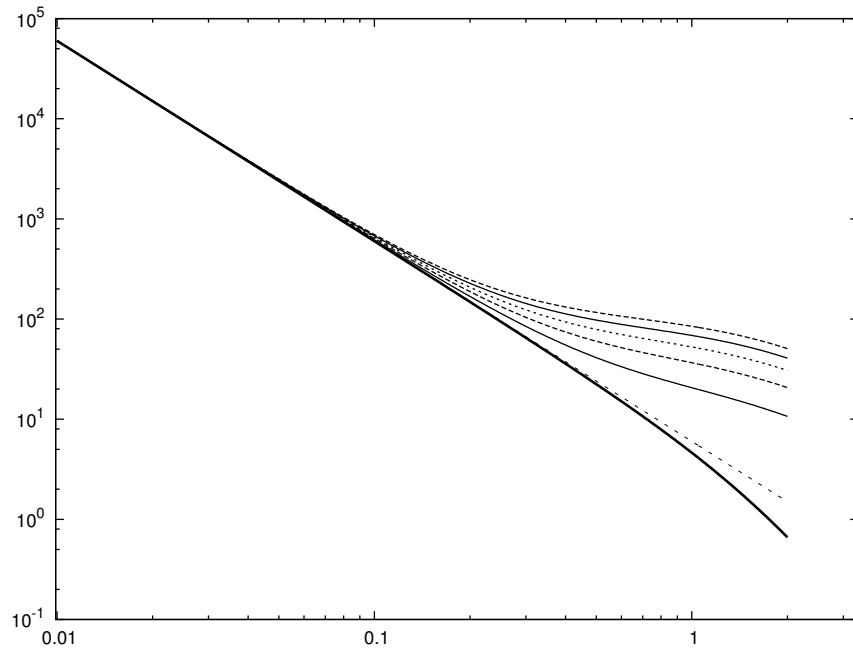Here we find $\kappa = \kappa^*(\gamma_{\text{MF}}\sigma^2)/(\sigma c)^2$, with the reduced value $\kappa^* = 0.288$.

Fig. 1. Log-log plot of $\tilde{g}^*(x)$ versus $x = q/c$ for $Lc = 100, 80, 60, 40$ and 20 from top; interfacial contribution $\Delta\phi_b^2 S_{\text{int}}^*(x)$, bottom; CWT limit, straight line.
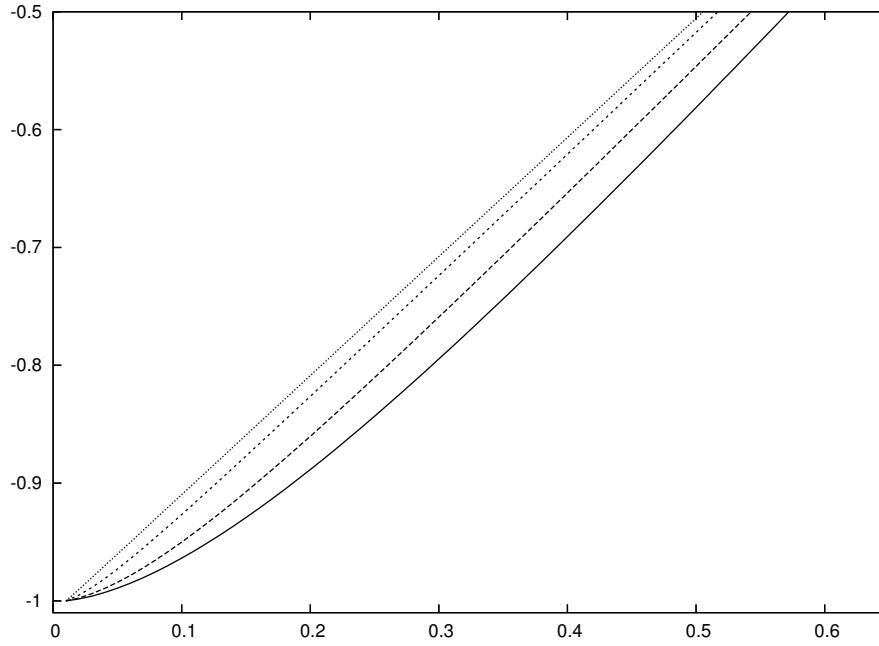
Fig. 2. $\gamma^{(1)}(\sigma/L_x)/|\gamma^{(1)}(0)|$ in terms of σ/L_x for $q_M/(2\pi c) = 1; 2; 5$ and 50 from bottom to top.

Surface tension

The contribution $\gamma^{(1)}$, given by (8), depends on the two bounds q_m and q_M of the wave vector q which are related to the relevant parameters of the interface: on the one hand $q_M/c = 2\pi/(\sigma c)$ where $1/(\sigma c)$ is the intrinsic width of the interface in unit σ, $q_M/c \in [1, \infty[$. On the other hand, $q_m/c = (2\pi)(L_x/c)$ where L_x is the system lateral size; hence $q_m/c = (q_M/c)(\sigma/L_x)$. Thus q_M/c appears as a natural parameter, with $q_M/c \in [2\pi, \infty]$ and $1/(q_M/c) \propto c \propto \sqrt{t}$. We can now re-write $\gamma^{(1*)}$ is a more convenient form ($\sigma/L_x \in \,]0, 1]$)

$$\gamma^{(1*)} = \frac{\pi}{2(q_M/c)^2}$$
$$\times \left[\tilde{\gamma}\left(4 + (q_M/c)^2\right) - \tilde{\gamma}\left(4 + \left(\frac{q_M}{c}\frac{\sigma}{L_x}\right)^2\right) \right] \quad (16)$$

(L_x/σ) is either the actual lateral system size or the scale at which γ is measured, for instance in a numerical simulation (see ref. [23]), but in any case does not depend on t. We can note that whatever the values of σ/L_x or (q_M/c), $\sigma^2\gamma^{(1)}$ remains finite and more precisely

$$\gamma^{(1*)}_{L_x\to\infty}(q_M/c \to \infty) \sim -\frac{6\pi}{q_M/c} \quad (17)$$

which $\to 0$ when $t \to 0$ as $t^{1/2}$. The results for $\sigma^2\gamma^{(1*)}$ are displayed in Fig. 2. We interpret $\sigma^2\gamma^{(1*)}(\sigma/L_x)$ as the q-dependent contribution to γ with $q = (2\pi\sigma/L_x)$. This means that the flat interface corresponding to the mean field approximation is obtained when no fluctuations at all are taken into account, namely for $q \sim q_M$. This differs from what is done in Ref. [13] (see also Ref. [24])

where the contribution to γ due to the surface fluctuations vanishes at $q \to 0$. The small q behavior of $\gamma^{(1*)}$ is easily obtained from (16) and yields

$$\gamma^{(1*)}_{q\to 0} \simeq \gamma^{(1*)}(0)$$
$$+ \frac{1}{8\pi}\left[(q\sigma)^2[a + \ln(c\sigma)] - 2(q\sigma)^2\ln(q\sigma)\right] \quad (18)$$

with $a = 3.48491$, from which we can deduce a crossover value of q given by $q_0\sigma = (c\sigma)e^{a/2}$, separating the q^2 behavior from the $(q\sigma)^2\ln(q\sigma)$ behavior obtained for $q < q_0$ and $q > q_0$ respectively. It is important to note first that we always get an increasing $\gamma^{(1)}(q)$ and secondly that since q_0 is proportional to c, we get a plateau (corresponding to the q^2 dependence) at small values of σ/L_x only when q_M/c takes small values, i.e. for the lowest temperatures (see figure 2. This behavior is in qualitative agreement with the simulation results of [23].

Notice that the term proportional to q^2 in the variation of $\gamma^{(1)}$ with q can be interpreted as resulting from the energy necessary to bend the interface, and should be related to κ obtained from the behavior of $S_{\text{int}}(q)$ (see Eq. (15)). This is not a priori the case since we do not expect a full coherence in the framework of a loop expansion between the energetic and structure quantities.

Concluding remarks

To conclude, we have shown in this work that the simple one-loop expansion of the grand potential in the the simplest inhomogeneous situation provides a qualitative but nevertheless coherent picture of the structure of the liquid vapor interface of simple liquids. We emphasize

that the spectrum of eigenstates resulting from the diagonalization of the second functional derivative of the effective Hamiltonian must be treated as a whole and one cannot take into account only the first bounded state as is sometimes done in the literature. Moreover, starting from a 3D Hamiltonian, and without invoking a phenomenological description of the interface, we recover the usual CWT surface Hamiltonian as the first approximate step. We also show that we can extract a rigidity bending factor which takes a positive value, in agreement with the requirement for the stability of the interface with respect to fluctuations.

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МЕТОД СТАТИСТИКО-ПОЛЬОВОЇ ТЕОРІЇ, ЗАСТОСОВАНИЙ ДО МІЖФАЗНОЇ ГРАНИЦІ РІДИНА–ПАРА

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Останнім часом поновився інтерес до використання методів статистико-польової теорії для опису рівноважних систем як в околі критичної точки, так і далеко від неї, зокрема в галузі фізики рідин. Ці роботи стосуються в загальному однорідних систем, хоча недавно в межахах такого підходу було розглянуто рідини поблизу твердої стінки. З іншого боку, був записаний ефективний гамільтоніан з сімейства теорії ϕ^4, що інтенсивно використовувався для опису неоднорідних систем поблизу границі між рівноважними фазами або для опису явища змочування. Ця робота присвячена теоретико-польовому опису міжфазної границі рідина-пара простих плинів. Ми починаємо з представлення великої статистичної суми, отриманої в результаті перетворення Габбарда–Стратоновича, яке приводить до точного формулювання проблеми без уведення ефективного гамільтоніана чи зв'язування поля з одночастинковою густиною рідини. З використанням плину твердих сфер як системи відліку та накладанням умови співіснування одержаний гамільтоніан дає звичайну теорію ϕ^4 без підгінного параметра. Важливим моментом є те, що так звана теорія капілярних хвиль виникає як однопетлеве наближення у функціональному розкладі гамільтоніана без використання додаткових феноменологічних міркувань.