

Statistical field theory for liquid vapor interface

V. Russier^{1*}, J.-M. Caillol^{2†}

¹ ICMPE, UMR 7182 CNRS and Université Paris Est 2–8 rue Henri Dunant, 94320 Thiais, France

² Laboratoire de Physique Théorique, UMR 8627 CNRS and Université de Paris Sud, bat. 210, 91405 Orsay Cedex, France

Received January 15, 2010, in final form February 26, 2010

A statistical field theory for an inhomogeneous liquid, a planar liquid/vapor interface, is devised from first principles. The grand canonical partition function is represented *via* a Hubbard-Stratonovitch transformation leading, close to the critical point, to the usual ϕ^4 scalar field theory which is then rigorously considered at the one-loop level. When further simplified it yields the well-known capillary wave theory without any *ad hoc* phenomenological parameter. Internal coherence of the one-loop approximation is discussed and good overall qualitative agreement with recent numerical simulations is stressed.

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

PACS: 61.30.Hn, 64.70.F, 68.03.Cd

1. Introduction

The structure in the interface between two fluid phases at coexistence plays a key role in many specific situations, such as, for instance, the wetting transition and related phenomena [1–7]. An understanding and proper description of this structure is undoubtedly a challenge that presents a great interest in itself from a theoretical point of view. For simple fluids, one of the key features of interfaces that separate subcritical phases at coexistence is the presence of thermally activated capillary waves [8] coupled with density fluctuations in the bulk. Since the pioneering work of Buff et al. [8] capillary waves have been widely studied and are usually described through the introduction of an *ad hoc* effective surface Hamiltonian, written as a functional of the interface height, $z_{\text{int}}(\vec{s})$, \vec{s} being the coordinate parallel to the interface in the case of a planar interface as considered henceforth. $H[z_{\text{int}}(\vec{s})]$ can be obtained through different ways and is most generally deduced from phenomenological arguments taking into account the interplay between gravity and surface tension effects. It is noteworthy that most works in this area are devoted to the wetting transitions where the Hamiltonian includes an external potential, say $W(z_{\text{int}}(\vec{s}))$, which pins the interface to a solid substrate.

The Hamiltonian $H[z_{\text{int}}(\vec{s})]$, can be treated in the framework of statistical field theoretical methods [2, 4], including renormalization group (RG) [9] techniques. For instance the hierarchical reference theory (HRT) has been recently generalized to inhomogeneous cases in order to deal with the wetting transition [7]. In the case of the liquid/vapor interface, when $H[z_{\text{int}}(\vec{s})]$ 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 $S_{\Delta z \Delta z}(q)$. Moreover, $3D \phi^4$ model in which the stochastic variable ϕ does not coincide with the height $z_{\text{int}}(\vec{s})$ was studied in refs [5, 6, 10, 11]. Alternative ways of deducing an effective Hamiltonian from a density functional theory (DFT) including the effect of gravity [12] or the local curvature of the interface [13, 14] have been also considered. Recently [15], a model for the density profile based on an extension of a displaced profile approximation, i.e. in which the profile is written as a function of $(z - z_{\text{int}}(\vec{s}))$, was considered.

*E-mail: russier@icmp.cnrs.fr

†E-mail: jean-michel.caillol@th.u-psud.fr

In addition, the model takes into account, together with the surface fluctuations described by the height $z_{\text{int}}(\vec{s})$, bulk phase fluctuations.

The purpose of the present work, which is an extension of a preliminary work [16], is to provide a simple description of the liquid / vapor interface of fluids in the framework of an exact statistical field theory. The latter is obtained from a Kac-Siegert-Stratonovich-Hubbard-Edwards (KSSHE) [17–22] transformation devised to rewrite the grand canonical partition function (GCPF) of the inhomogeneous fluid as the partition function of a statistical field theory involving the stochastic real field ϕ . The method is an alternative to the so-called collective variables method developed notably by I. Mryglod and coworkers [23, 24], that was mainly used for homogeneous fluids in [23–25] and is considered here in studying a planar interface. It is important to mention that the present work is not based on the determination of an effective surface hamiltonian, conversely to [26, 27]. The theory is studied at the one-loop level where everything can be achieved analytically. The links between correlations of the field and density correlations are established as well as the expressions for the surface tension and the surface structure factor are presented. Here the surface tension is not assimilated to the stiffness factor of the effective surface Hamiltonian gradient term [26] but conversely is the surface contribution of the logarithm of the GCPF. Technically, this is done *via* the determination of the eigenvalues and eigenfunctions of the second functional derivative of the mean field KSSHE Hamiltonian, which can be done exactly, as well known, for the one-dimensional kink [28]. The whole spectrum of eigenstates being taken into account proves to be of the outmost importance in obtaining the correct result. Thus we obtain a satisfying picture of the liquid vapor interface, at least qualitatively, even at this simple level of description. One of the salient points of our work is that we recover both the CWT and its first extension, namely the appearance of the bending rigidity factor k and the coupling between surface and bulk density correlations in $S(q)$, without invoking any *ad hoc* phenomenology.

It is a pleasure for the authors to dedicate this paper to Ihor Mryglod to celebrate his fiftieth anniversary. One of the authors (JMC) acknowledges many interesting discussions with Ihor, about science and other topics, either in Orsay University or L'viv ICMP on the occasion of many meetings and collaborations of French and Ukrainian teams.

Bon anniversaire Ihor et longue vie à toi !

2. KSSHE transform and mean-field approximation

The important steps leading to the appropriate statistical field theory for a liquid are outlined in Appendix A; the interested reader is referred to [18, 23–25] for deeper details and to [29] for an alternative formulation. We consider a simple fluid whose pair interaction potential includes a hard sphere (HS) repulsive part and a soft attractive part, denoted by $v(r)$. 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. $\tilde{w}(k) > 0$). We work in the grand canonical ensemble, namely at constant chemical potential $\nu = \beta\mu$, and we consider the grand canonical partition function (GCPF) related to the grand potential $\Xi = \exp(-\beta\Omega)$. Following the notations of appendix A we obtain for Ξ

$$\begin{aligned}\Xi[\nu] &= \frac{1}{N_w} \int \mathcal{D}\phi \exp(-H[\phi]), \\ H &= \frac{1}{2} \phi \cdot w^{-1} \cdot \phi - \ln(\Xi_{\text{HS}}[\bar{\nu} + \phi]),\end{aligned}\tag{1}$$

where ϕ is a real scalar field, $\mathcal{D}\phi$ a functional integration measure, $\bar{\nu} = \nu - w(0)/2$ and, finally, $\Xi_{\text{HS}}[\nu]$ is the hard sphere grand partition functional of the local chemical potential $\nu(\vec{r})$. A Landau-Ginzburg form is obtained from a functional Taylor expansion of $\ln(\Xi_{\text{HS}})$ around a conveniently chosen reference chemical potential of the hard sphere fluid, ν_0 (see Appendix A). The propagator is expanded up to order k^2 in Fourier space and we are left with

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

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

$$B(x) = \int dy w^{-1}(x, y) \Delta \nu(y) + \rho_{\text{HS}}[\nu_0](x) \quad \text{with} \quad \Delta \nu = \bar{\nu} - \nu_0, \quad (2c)$$

where the coupling constants K_0, K_2 and u_n depend only on the equation of state of the hard sphere fluid and the potential w (see below). This formulation permits an exact mapping between the densities and their correlations on the one hand and the mean value and the correlations of the field on the other hand, as exemplified in equation (A-13) in the appendix. For instance at 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 value of ν_0 is chosen in such a way that $u_3(\nu_0)$ vanishes and the coexistence condition between the liquid and vapor phases in the absence of external field is $B = 0$. K_0 is related to the deviation from the critical temperature: $t = (T_c - T)/T_c \propto (-K_0)$.

In the inhomogeneous system, we assume a special realization of the two phases coexistence: we explicitly impose the occurrence 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 system is supposed to be bounded in the direction z according to $(z_0 - L) < z < (z_0 + L)$, L being macroscopically large though formally finite. The localization of the interface is obtained through the introduction of a small valued external field $h_{\text{ext}}(z - z_0)$, odd in $(z - z_0)$. Since the mean field profile takes constant values in both bulk phases, so is the case for h_{ext} which therefore plays the same role as the truncated gravitational field used in [12]. This leads to a constraint on the averaged field profile although this method differs from that of [27] since we do not seek a collective variable because we still deal with the GCPF of the whole system. The advantage of our choice will be shown below; we emphasize that we do not aim to study gravitational effects but rather to fix the location of the interface at $z = z_0$. The inhomogeneous mean field theory or saddle point equation, $\delta H[\phi]/\delta \phi = h_{\text{ext}}(z - z_0)$, is solved by exploiting the fact that we look for a monotonous solution for the mean field profile $\phi_c(z) = \phi_{\text{MF}}(z)/\phi_b$, where ϕ_b is the value of $\phi_{\text{MF}}(z)$ when $z \rightarrow z_0 + L$, and by expanding h_{ext} as a function of $\phi_c(z)$, namely $h_{\text{ext}}(z) = h_{\text{ext}}(\phi_c(z))$. The mean field equation then reads

$$K_2 \frac{\partial^2 \phi_{\text{MF}}}{\partial z^2} = K_0 \phi_{\text{MF}} + \frac{\partial V}{\partial \phi}(\phi_{\text{MF}}) - h_{\text{ext}}(\phi_c). \quad (3)$$

Since we consider a local approximation for the $n \geq 3$ HS kernels (see equation (A-14)), the r.h.s. of equation (3) is a polynomial in $\phi_{\text{MF}}(z - z_0)$. Limiting $V(\phi)$ to the first non-vanishing term, namely $V(\phi) = (u_4/4!)\phi^4$, the analytical form for ϕ_{MF} is not modified by the introduction of an external field if the latter expands as $h(\phi_c) = h_1 \phi_c + (h_3/3!)\phi_c^3$ (h_1, h_3 constants), as already noted by Zittartz [30] when $h(\phi_c) = h_1 \phi_c$ (This result holds in a more general way for a potential $V(\phi)$ even in ϕ and an external field odd in ϕ_c where the highest power of $V(\phi)$ is that of $h(\phi_c)$ plus one). The solution of the mean field equation in the presence of external field, $\phi_{\text{MF}}(K_2, K_0, u_4, h_{\text{ext}})$, coincides with the solution in the absence of external field, with modified values of the coupling constants K_0 and u_4 .

$$\begin{aligned} \phi_{\text{MF}}^{(K_2, K_0, u_4; h_{\text{ext}})}(z) &= \phi_{\text{MF}}^{(K_2, K'_0, u'_4; 0)}(z), & K'_0 &= K_0 - \delta K_0, & u'_4 &= u_4 - \delta u_4 \\ \text{with } \delta K_0 &= h_1 \left(\frac{u'_4}{-6K'_0} \right)^{1/2} & \text{and } \delta u_4 &= h_3 \left(\frac{u'_4}{-6K'_0} \right)^{3/2}. \end{aligned} \quad (4)$$

The solution of equation (3) is $\phi_{\text{MF}}(z) = \phi_b \phi_c((z - z_0)/l)$ with $\phi_c(x) = \tanh(x)$, $\phi_b = (-6K'_0/u'_4)^{1/2}$ and $l = (2K_2/-K'_0)^{1/2}$ is the bulk correlation length which also coincides with the intrinsic interface width. Contrary to the situation encountered in wetting problems, as for instance in [27], we do not need to approximate the mean field solution in our case. We emphasize that we deal only with subcritical temperatures where $K'_0 < 0$. We first have to check the mapping between the physical external field seen by the liquid, say $\Psi(z) = \beta V_{\text{ext}}(z)$, and the external field which enters the

effective Hamiltonian of equation (2a). Thus we have to solve

$$B(1) = B_0 - \int w^{-1}(1, 2) \Psi_{\text{ext}}(2) d2 \equiv h_{\text{ext}}(1). \quad (5)$$

B_0 given by equation (2c) is the constant external field appearing in the effective Hamiltonian when h_{ext} vanishes. The coexistence condition at constant chemical potential still reads $B_0 = 0$. Since the propagator has been expanded up to order k^2 (see appendix A), w^{-1} is given in real space, at the same order of approximation, by

$$w^{-1}(1, 2) = \frac{1}{\tilde{w}_0} \left[1 + \frac{\tilde{w}_2}{\tilde{w}_0} \Delta_1 \right] \delta(1, 2), \quad (6)$$

where \tilde{w}_0 and \tilde{w}_2 denote the coefficients of the expansion at order k^2 of the Fourier transform, $\tilde{w}(k)$, of w . By restricting ourselves to functions depending only upon z , we have

$$\int w^{-1}(1, 2) \Psi_{\text{ext}}(2) d2 = \frac{1}{\tilde{w}_0} \left[1 + \frac{\tilde{w}_2}{\tilde{w}_0} \frac{\partial^2}{\partial z_1^2} \right] \Psi_{\text{ext}}(1) = h_{\text{ext}}(z_1). \quad (7)$$

We introduce the bulk correlation length, l and we look for a solution depending on $t = \phi_c(z/l)$ for both $h_{\text{ext}}(z_1)$ and $\Psi_{\text{ext}}(z_1)$. Equation (7) then reads

$$\left((1-t^2)^2 \frac{\partial^2}{\partial t^2} - 2t(1-t^2) \frac{\partial}{\partial t} + l^2 \frac{\tilde{w}_0}{\tilde{w}_2} \right) \Psi = -\frac{\tilde{w}_0^2}{\tilde{w}_2} l^2 h_{\text{ext}}. \quad (8)$$

A one to one mapping with h_{ext} limited to the third power in ϕ_c is obtained when $\partial^2 \Psi / \partial t^2 = 0$ and we get

$$\begin{aligned} \Psi(z) &= \Psi_1 \phi_c(z); & h_{\text{ext}}(z) &= h_1 \phi_c(z) + \frac{h_3}{3!} \phi_c(z)^3, \\ h_1 &= -\Psi_1 \frac{1}{\tilde{w}_0} \left(1 - \frac{2}{l^2} \frac{\tilde{w}_2}{\tilde{w}_0} \right), \\ h_3 &= -\Psi_1 \frac{2}{l^2} \frac{\tilde{w}_2}{\tilde{w}_0}. \end{aligned} \quad (9)$$

Formally l is finite but clearly the present approach should be valid only but in the vicinity of the critical point where $l \rightarrow \infty$ and we can therefore neglect the term h_3 .

The mean field surface tension follows from the identity $\Omega_{\text{MF}}[\nu] = H[\phi_{\text{MF}}(z)]$ which is easily calculated by using both the equation satisfied by ϕ_{MF} and the expression of the external field contribution which takes a simple form with the particular choice for h_{ext} , with the result

$$\beta \sigma^2 \gamma_{\text{MF}} = 4\sigma^2 (-2K_2 K_0' / u_4')^{1/2} + 2\sigma^2 \left(\frac{3K_2}{u_4'} \right)^{1/2} h_1 \left(1 + \frac{h_3}{3h_1} \right)$$

which is similar to the expression given by Brilliantov [11] in the absence of the external field and differs from that given by Zittartz [30] due to a different choice for the external field as a function of ϕ_c . When $h_3 = 0$ and $h_1 \rightarrow 0$ at finite K_0 we get

$$\beta \sigma^2 \gamma_{\text{MF}}(K_0, K_2, h_1 \rightarrow 0) \rightarrow \beta \sigma^2 \gamma_{\text{MF}}(K_0, K_2, h_1 = 0) + \frac{\sigma^2 4(K_2)^{1/2} \phi_b}{(-3K_0)^{1/2}} h_1. \quad (10)$$

For $t \rightarrow 0$, one recovers the mean field exponent, $\gamma_{\text{MF}} \sim t^{3/2}$.

3. One loop equations

In order to go beyond the mean-field approximation, we expand the Hamiltonian about $\phi_{\text{MF}}(z)$ and consider the Gaussian approximation. Hence, we drop the cubic term in the external field (i.e. we set $h_3 = 0$) and, in order to unclutter notations, we define $\bar{h}_1 = h_1/\phi_b$. Without any loss of generality, we also choose $z_0 = 0$. The first correction stems from the second order term and we have ($z_0 = 0$),

$$H[\phi = \phi_{\text{MF}} + \chi] \simeq H[\phi_{\text{MF}}] + \frac{1}{2} \int \chi(1) H^{(2)}(1, 2) \chi(2) d1d2. \quad (11)$$

The operator $H^{(2)} = \delta^2 H / \delta\phi(1) \delta\phi(2)$ is diagonalized, after a Fourier transform parallel to the surface, in the set of eigenfunctions φ_λ solution of the eigenvalues equation ($\epsilon_\lambda = K_2(q^2 + \bar{h}_1 + \omega_\lambda/l^2)$)

$$K_2 \left(-\frac{\partial^2}{\partial z^{*2}} + 6(\tanh^2(z^*) - 1) + (4 - \omega_\lambda) \right) \varphi_\lambda(z^*) = 0, \quad z^* = z/l \quad (12)$$

the solutions of which are known [5, 30, 31]. We emphasize that keeping only the linear term in the external field leads to the same Schrodinger-like equation (12) as in the absence of external field and the only change is a shift of the eigenvalues ϵ_λ of \bar{h}_1 . The spectrum of eigenfunctions includes two bound states, $\varphi_0 = C_0 / \cosh^2(z/l)$ and $\varphi_1 = C_1 \sinh(z/l) / \cosh^2(z/l)$, with $\omega_0 = 0$, $\omega_1 = 3$ respectively and a subset of unbounded states, or continuum spectrum $\varphi_k(z)$, with $kl = \sqrt{\omega_k - 4}$ which behave as plane waves in the bulk phases, i.e. far from the interface, and are given by

$$\varphi_k(z) = C(k) e^{ikz} [2 - k^2 l^2 - 3i kl \tanh(z/l) + 3(\tanh^2(z/l) - 1)]. \quad (13)$$

Notice that the shift of eigenvalues due to the external field is of crucial importance especially for the lowest bounded state φ_0 the energy of which ϵ_0 tends to a finite value, $K_2 \bar{h}_1$ when $q \rightarrow 0$. As we shall see in the sequel this corresponds to a pinning of the interface by the field. It is important to note that $\varphi_0(z) \propto \partial\phi_{\text{MF}}(z)/\partial z$. The constants C_0 , C_1 and $C(k)$ are determined in order to normalize the φ_λ on the interval $[-L, L]$. The whole spectrum of eigenstates should then be orthogonalized. For the bound states this is a direct consequence of the eigenvalues equation (12) in the limit $L/l \rightarrow \infty$, i.e. disregarding terms of order $\exp(-2L/l)$. On the other hand the orthogonalization of the subset of unbounded eigenstates is no more a consequence equation (12) but rather follows from the boundary condition

$$[\varphi_k \varphi_{k'}^*]_{-L}^L = 0 \quad \text{for} \quad k \neq k' \quad (14)$$

from which we get the non-trivial dispersion relation leading to the density of states ($x = kl$)

$$n(k) = \frac{L}{\pi} - \frac{l}{\pi} \left[\frac{1}{(1+x^2)} + \frac{2}{(4+x^2)} \right] = \frac{L}{\pi} + l f(x). \quad (15)$$

The closure relation then follows

$$\int_{-\infty}^{+\infty} \frac{dk}{2\pi} \left(n(k) |\varphi_k(z)|^2 - 1 \right) + \varphi_0^2(z) + \varphi_1^2(z) = 0. \quad (16)$$

It is important to note that $\int_{-\infty}^{\infty} f(x) dx = -2$ which proved useful in all calculations. Zittartz [30] has already got this density of states but without explicitly mentioning the need of the orthogonalization. In [32] Evans outlined the way to deal with the liquid-vapor interface in the framework of statistical field theory, also at the one loop level; however, the continuous spectrum was only qualitatively evoked and no particular attention was paid to the orthogonalization problem which should be performed on the formally *finite* system. In [33] a similar kind of dispersion relation was obtained in the modeling 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 $\chi(\vec{r})$ in the basis which diagonalizes the operator $H^{(2)}$, namely a Fourier transform in the \vec{s} -direction and a projection on the $\varphi_\lambda(z)$ where $\{\lambda\} = \{n = 0, 1; k\}$ denotes the whole spectrum of eigenstates. From usual gaussian functional integrals [34] we get

$$\begin{aligned} \ln(\Xi) = & -H[\phi_{\text{MF}}] + \frac{V}{2} \int \frac{d\vec{k}}{(2\pi)^3} \ln \left(\frac{\hat{w}^{-1}(k)}{\epsilon_k(q)} \right) \\ & - \frac{S}{2} \int \frac{d\vec{q}}{(2\pi)^2} \left(\sum_n \ln(\epsilon_n(q)) + \int dk f(kl) \ln(\epsilon_k(q)) \right), \end{aligned} \quad (17)$$

where the ϵ_k coincide with the eigenvalues of the second functional derivative of the Hamiltonian for the ϕ^4 homogeneous model taken at $\phi = \phi_{\text{MF}}(\pm L)$. Therefore, the volume term of $\ln(\Xi)$ in (17) is nothing but βpV at the one loop approximation [25]. We finally write the surface term of $\ln(\Xi)$ in terms of the surface tension $\gamma = [\ln(\Xi_b) - \ln(\Xi)]/S = \gamma_{\text{MF}} + \gamma^{(1)}$. As already mentioned, this expression for γ differs from the definition as the stiffness factor of the effective surface Hamiltonian (see for instance [26]) although the two routes coincide at the mean field level. We obtain ($\gamma^{(1*)} = \beta\gamma^{(1)}\sigma^2$)

$$\gamma^{(1*)} = \frac{1}{8\pi} \left[(t-1) \ln\left(1 - \frac{2}{\sqrt{t+1}}\right) + (t-4) \ln\left(1 - \frac{4}{\sqrt{t+2}}\right) - 6\sqrt{t} \right]_{a+(q_m l)^2}^{a+(q_M l)^2}, \quad (18)$$

where q_m and q_M are the lower and the upper bound of the integral over q and $a = (4 + \bar{h}_1)$, respectively. A similar result was obtained in [30] for a spin model. This result differs from that obtained in [4] where only the $n = 0$ eigenstate is kept. In the limit $\bar{h}_1 \rightarrow 0$, we get

$$\gamma^{(1*)}(\bar{h}_1) \rightarrow \gamma^{(1*)}(\bar{h}_1 = 0) - (1/8\pi)\bar{h}_1 \ln(\bar{h}_1). \quad (19)$$

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

$$\sum_\lambda \frac{\varphi_\lambda(z_1)\varphi_\lambda^*(z_2)}{\epsilon_\lambda(q)} = \sum_{n=0,1} \frac{\varphi_n(z_1)\varphi_n(z_2)}{\epsilon_n(q)} + \int \rho(k) \frac{\varphi_k(z_1)\varphi_k^*(z_2)}{\epsilon_k(q)} dk.$$

A contribution of the integral over k exactly cancels 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 ($z_{>,<} = \sup, \inf(z_1, z_2)$)

$$\begin{aligned} G_\phi(z_1, z_2, q) = & \frac{9l}{2K_2} \frac{\exp(-|z_{12}|(x^2+4)^{1/2}/l)}{x^2(x^2+3)(x^2+4)^{1/2}} \left[1 + x^2/3 + (x^2+4)^{1/2} \tanh(z_{>}/l) + \tanh^2(z_{>}/l) \right] \\ & \times \left[1 + x^2/3 - (x^2+4)^{1/2} \tanh(z_{<}/l) + \tanh^2(z_{<}/l) \right], \end{aligned} \quad (20)$$

where $x^2 = (q^2 + \bar{h}_1)l^2$. Notice that formally this expression coincides with that obtained in the absence of the external field, the only difference being the definition of x which takes a finite value, \bar{h}_1 when $q \rightarrow 0$.

4. Results and discussion

4.1. 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 normalization. If we keep only this first eigenstate, the expansion of χ reads $\chi(\vec{s}, z) = \xi(\vec{s})\varphi_0(z)$. Hence the field takes the form $\phi(z) = \phi_c(z - z_{\text{int}}(\vec{s}))$ and only the linear term in the expansion of ϕ with respect to z_{int} remains. This indeed corresponds to the so-called rigidly displaced profile approximation, where $z_{\text{int}} = -a\xi(\vec{s})$ represents the fluctuating location of the interface. The corresponding contribution to H is a functional of $z_{\text{int}}(\vec{s})$ which defines an effective surface Hamiltonian given by

$$H_s^{(0)}[z_{\text{int}}(\vec{s})] = \frac{K_2}{2a^2} \int d\vec{s} [(\partial_{\vec{s}}(z_{\text{int}}(s))^2 + \bar{h}_1 z_{\text{int}}(s)^2), \quad (21)$$

where we have used $\epsilon_0 = K_2(q^2 + \bar{h}_1)$ since $\omega_0 = 0$. This Hamiltonian pertains to the capillary wave models [12, 35–37]. In general, the capillary wave Hamiltonian is obtained either from phenomenological arguments [35] or by restricting the fluctuations beyond the mean field level to those deduced from a rigidly displaced mean field profile [36]. In [12] a formulation based upon the direct correlation function of the liquid state theory is used. In [38] a supplementary $z_{\text{int}}(s)^4$ term in the surface Hamiltonian (21) was introduced in order to account for curvature effects of the interface; this additional term should vanish with the external field, [37] and in any case cannot be generated in the framework a one loop scheme. From the normalization of φ_0 and from the analytic form of the mean field profile we deduce $K_2/a^2 = \sigma^2\beta\gamma_{\text{MF}} - \sigma^2l\phi_b^2\bar{h}_1$ and accordingly we rewrite (21) in the form

$$H_s^{(0)} = \frac{1}{2} [\beta\gamma_{\text{MF}} - \sigma^2l\phi_b^2\bar{h}_1] \int d\vec{s} [(\partial_{\vec{s}}(z_{\text{int}}(\vec{s})))^2 + \bar{h}_1 z_{\text{int}}(\vec{s})^2] \quad (22)$$

which exactly coincides with the usual effective surface Hamiltonian $H_{\text{CWT}}[z_{\text{int}}(\vec{s})]$ of the CWT theory for the free surface, when the external field vanishes. Therefore, in the limit $h_1 \rightarrow 0$ we obtain the CWT as the lowest approximation beyond the mean field approximation without invoking phenomenological arguments. The structure is characterized by the height-height correlation function, $\langle z_{\text{int}}(\vec{s}_1)z_{\text{int}}(\vec{s}_2) \rangle$ or its Fourier transform parallel to the surface which defines the surface structure factor, $S_{\Delta z \Delta z}(q)$, where $z_{\text{int}}(\vec{s})$ is the location of the interface relative to its mean value. We consider $\int \chi(\vec{s}, z) dz / \Delta\phi_b$, where $\Delta\phi_b = \phi_{\text{MF}}(L) - \phi_{\text{MF}}(-L)$, as a measure of the instantaneous location of the surface at \vec{s} , which amounts to define the location of the surface from a constraint on the integral of χ , as is done in [15] for the density profile. We are then led to identify $S_{\Delta z \Delta z}(q) = (\Delta\phi_b)^{-2} \int G_\phi(z_1, z_2, q) dz_1 dz_2$, which corresponds to the S_{ic} used in [15]. It is important to notice that the coupling with the bulk fluctuations is included in the present formulation through the eigenstates of the continuum. We also introduce the effective surface width, or surface corrugation, $\sigma^{\text{eff}} = \sqrt{\langle z_{\text{int}}(\vec{s}_1)z_{\text{int}}(\vec{s}_1) \rangle}$. Henceforth we consider only small values of \bar{h}_1 and more precisely we relate the value of \bar{h}_1 to an effective lateral size of system, according to $\bar{h}_1 \sim L_x^{-2}$ as it will be justified from the analysis of the capillary wave limit. The behavior of $S_{\Delta z \Delta z}(q)$ is analyzed from the function $\tilde{g}(q) = \int dz_1 \int dz_2 G_\phi(z_1, z_2, q)$. From (20) for the leading term of $G_\phi(z_1, z_2, q)$ when $q \rightarrow 0$ we get

$$G_\phi(z_1, z_2, q \rightarrow 0) \simeq \frac{1}{K_2(q^2 + \bar{h}_1)} \varphi_0(z_1)\varphi_0(z_2) + \frac{3l}{2K_2} \frac{\bar{h}_1}{q^2 + \bar{h}_1} e^{-2|z_{12}|/l} [f(z_1, z_2)]. \quad (23)$$

The first term of the r.h.s. of equation (23) corresponds to the *CWT* limit, especially when $\bar{h}_1 = 0$, and the correction, which vanishes at $\bar{h}_1 = 0$, plays a role only far from the interface where $\varphi_0(z_1)\varphi_0(z_2)$ is negligible and moreover when the two particles are on the same side of the interface, i.e. when $e^{-2|z_{12}|/l}$ is not negligible. Thus we can rewrite the $q \rightarrow 0$ behavior of $G_\phi(z_1, z_2, q)$ as

$$G_\phi(z_1, z_2, q \rightarrow 0) \simeq \frac{1}{K_2(q^2 + \bar{h}_1)} \varphi_0(z_1)\varphi_0(z_2) + \frac{l}{2K_2} f e^{-2|z_{12}|/l}, \quad (24)$$

where f takes a constant value, $f = 1$, when both $|z_1|, |z_2| \gg l$ and are of the same sign. The second term of the r.h.s. of (24) is nothing but the limit at $q \rightarrow 0$ of the bulk correlation function and is not to be included in the capillary limit of the model. In any case, for sufficiently small

values of \bar{h}_1 , the bulk contribution to equation (24) becomes negligible at $q = 0$. This is made more precise hereinafter concerning the behavior of $S_{\Delta z \Delta z}$. Let us denote by G_{CW} the first term of the r.h.s. of equation (24) and by $\tilde{g}_{\text{CW}}(q)$ its integral over z_1 and z_2 . It is easy to show from the relation already used between the normalization of $\varphi_0(z)$ and γ_{MF} that

$$\frac{1}{(\Delta\phi_b)^2} \tilde{g}_{\text{CW}}(q \rightarrow 0) \rightarrow \frac{1}{(\gamma_{\text{MF}} - \sigma^2 l \phi_b^2 \bar{h}_1)(q^2 + \bar{h}_1)}. \quad (25)$$

In the limit $\bar{h}_1 = 0$ this is exactly the CWT behavior, leading to the well known logarithmic divergence of the squared surface corrugation for which one gets $(\sigma^{\text{eff}})^2 = (4\pi\gamma_{\text{MF}})^{-1} \ln(q_M^2/q_m^2)$. The effect of the external field is to make the integral over q entering the determination of σ^{eff} finite at $q \rightarrow 0$ with the result

$$(\sigma^{\text{eff}})^2 = \frac{1}{4\pi\beta\gamma_{\text{MF}}} \ln\left(\frac{(2\pi)^2}{\sigma^2 \bar{h}_1}\right) [1 + O(\sigma^2 \bar{h}_1)], \quad (26)$$

where we have assimilated q_M to the inverse of the molecular size, $2\pi/\sigma$. Since the result for the CW at the free interface in the absence of external field is a logarithmic divergence with the lateral size, $\sim \ln(\sigma/L_x)$ [8], this shows that, as we have already mentioned, the effect of the external field is to pin the interface in such a way that the capillary wave is restricted to a lateral scale $L_x \sim \bar{h}_1^{-(1/2)}$. It can be shown from (20) 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

$$S_{\Delta z \Delta z}(q) \simeq \frac{2L}{\Delta\Phi^2} \int G_b(q, z_{12}) dz_{12} + \frac{1 + (\sigma^2 l \phi_b^2 \gamma_{\text{MF}}) \bar{h}_1}{\gamma_{\text{MF}}(q^2 + \bar{h}_1)} + O(\bar{h}_1^2), \quad (27)$$

where $\Delta\Phi = \Phi_l - \Phi_g$ denotes the difference between the mean-field values in the two phases. Given that the bulk term leads to a constant when $q \rightarrow 0$, we see that (27) 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

$$(q_s^2 + \bar{h}_1) \sim \frac{\Delta\Phi^2}{2L \beta \gamma_{\text{MF}} K_2 \int G_b(q, z_{12}) dz_{12}}. \quad (28)$$

We see that this cross-over behavior holds only if \bar{h}_1 is negligible compared to the r.h.s. of equation (28) or in other words

$$\bar{h}_1 l^2 < \frac{l}{2L} \frac{16\phi_b^2 l K_2}{\beta \gamma_{\text{MF}} l^2}$$

and confirms the above mentioned separation of the capillary behavior from the bulk correlations when this condition is fulfilled. We emphasize that $\bar{h}_1^{1/2}$ can be understood as the inverse of an effective lateral size pinning the interface. The cross-over like behavior resulting from (28) is in agreement with that of [15, 39, 40]; 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 (27) we can drop exactly the bulk contribution, and doing this we define a purely interfacial contribution to $S_{\Delta z \Delta z}(q)$ (see figure 1).

$$S_{\text{int}}(q) = S_{\Delta z \Delta z}(q) - (2L/\Delta\phi_b^2) \int G_b(q, z_{12}) dz_{12}. \quad (29)$$

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 $S_{\Delta z \Delta z}(q)$. At this point, since we focus on the deviation from the capillary-like behavior, we can consider $\bar{h}_1 = 0$. 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,

$$\kappa = \lim_{q \rightarrow 0} ((1/q^2)\beta(q)) \simeq ((1/q^2)\beta(q)) \quad (30)$$

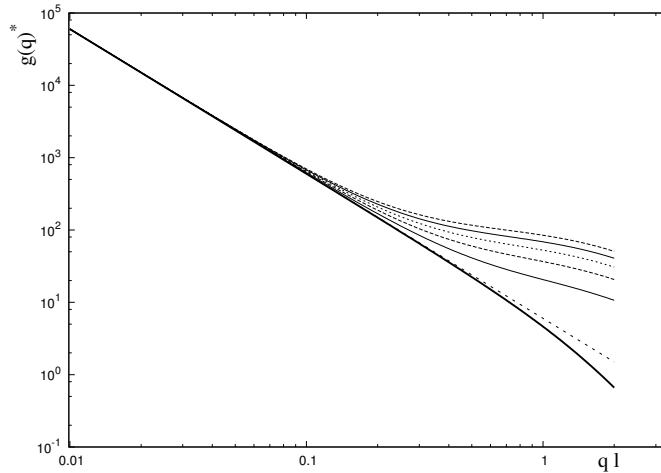


Figure 1. Log-log plot of $\tilde{g}^*(x)$ versus $x = ql$ for $\bar{h}_1 = 0$ and $L/l = 100, 80, 60, 40$ and 20 from top; interfacial contribution $\Delta\phi_0^2 S_{\text{int}}^*(x)$, bottom; CWT limit, straight line.

which takes a positive value, as it should be for the stability of the interface [14], as is also found from the simulation results of [40] after a separation between bulk density correlations and interface fluctuations. 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 $\kappa = \kappa^*(\gamma_{\text{MF}}\sigma^2)/(\sigma/l)^2$, with the reduced value $\kappa^* = 0.288$.

4.2. Surface tension

In this section we focus on the behavior of the one loop contribution to the surface tension γ in the case $\bar{h}_1 = 0$, since its dependence on \bar{h}_1 vanishes (see equation (19)). The contribution $\gamma^{(1)}$, given by (18), 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 $lq_M = 2\pi l/\sigma$ where l/σ is the intrinsic width of the interface in unit σ , $lq_M \in [1, \infty]$. On the other hand, $lq_m = (2\pi l/L_x)$ where L_x is the system actual lateral size; hence $lq_m = (lq_M)(\sigma/L_x)$. Thus lq_M appears as a natural parameter, with $lq_M \in [2\pi, \infty]$ and $1/(lq_M) \propto \sqrt{t}$. We can now re-write $\gamma^{(1*)}$ in a more convenient form ($\sigma/L_x \in]0, 1[$)

$$\gamma^{(1*)} = \frac{\pi}{2(lq_M)^2} \left[\tilde{\gamma} (4 + (lq_M)^2) - \tilde{\gamma} \left(4 + (lq_M \frac{\sigma}{L_x})^2 \right) \right], \quad (31)$$

(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 [41]), but in any case does not depend on t . We can note that whatever the values of σ/L_x or (lq_M) , $\sigma^2\gamma^{(1)}$ remains finite and more precisely

$$\gamma_{L_x \rightarrow \infty}^{(1*)}(lq_M \rightarrow \infty) \sim -\frac{6\pi}{lq_M} \quad (32)$$

which $\rightarrow 0$ when $t \rightarrow 0$ as $t^{1/2}$. The results for $\sigma^2\gamma^{(1*)}$ are displayed in figure 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 [14] (see also [42]) where the contribution to γ due to the surface fluctuations vanishes at $q \rightarrow 0$. The small q behavior

of $\gamma^{(1*)}$ is easily obtained from (31) and yields

$$\gamma_{q \rightarrow 0}^{(1*)} \simeq \gamma^{(1*)}(0) + \frac{1}{8\pi} [(q\sigma)^2 [a + \ln(\sigma/l)] - 2(q\sigma)^2 \ln(q\sigma)] \quad \text{with} \quad a = 3.48491 \quad (33)$$

from which we can deduce a crossover value of q given by $q_0\sigma = (\sigma/l)e^{a/2}$, separating the q^2 behavior from the $(q\sigma)^2 \ln(q\sigma)$ behavior obtained for $q < q_0$ and $q > q_0$ respectively. Firstly, it is important to note that we always get an increasing $\gamma^{(1)}(q)$ and secondly that since q_0 is proportional to l^{-1} , we get a plateau (corresponding to the q^2 dependence) at small values of σ/L_x only when lq_M takes small values, i.e. for the lowest temperatures (see figure 2). This behavior is in qualitative agreement with the simulation results of [41]. 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 equation (30)). 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.

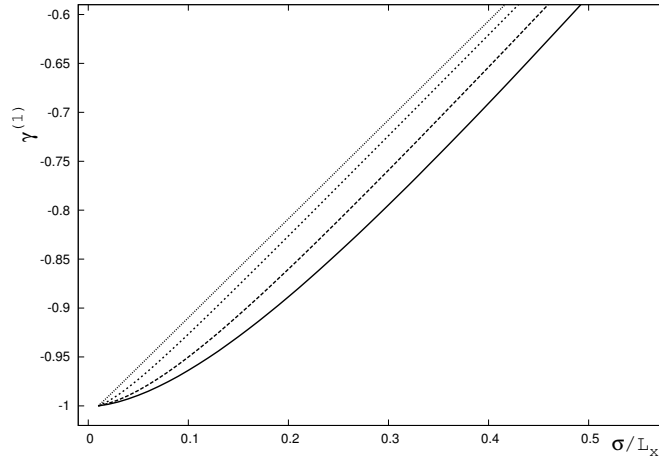


Figure 2. $\gamma^{(1)}(\sigma/L_x)/|\gamma^{(1)}(0)|$ in terms of σ/L_x for $lq_M/(2\pi) = 1; 2; 5$ and 50 from bottom to top.

4.3. Density profile and density correlation function

Now we go back to the mapping between the averaged field, ϕ , and the density in the fluid, ρ on the one hand and between the field and the two body density correlation function $G_\rho^{(2)T}$ on the other hand. Formally we have from equation (A-13)

$$\begin{aligned} \rho(1) &= \rho_{\text{HS}}[\nu_0](1) - h_{\text{ext}}(1) + \int w^{-1}(1, 2)\phi_{\text{MF}}(2)d2, \\ G_\rho^{(2)T}(1, 2) &= \iint w^{-1}(1, 1')w^{-1}(2, 2')G_\phi(1', 2')d1'd2' - w^{-1}(1, 2). \end{aligned} \quad (34)$$

We recall that $G_\rho^{(2)T}(1, 2)$ is $\rho(1)\rho(2)h(1, 2) + \rho(1)\delta(1, 2)$ where $h(1, 2)$ is the usual total correlation function of liquid state theory[43]. We easily get

$$\rho(1) = \rho_{\text{HS}}(\nu_0) + \Delta\rho_1\phi_c(z_1) + \Delta\rho_3\phi_c(z_1)^3, \quad (35)$$

where

$$\begin{aligned}\Delta\rho_1 &= \phi_b \left[\frac{1}{\tilde{w}_0} - \frac{\tilde{w}_2}{\tilde{w}_0^2 l^2} - \bar{h}_1 \right], \\ \Delta\rho_3 &= \phi_b \frac{\tilde{w}_2}{\tilde{w}_0^2 l^2}.\end{aligned}\tag{36}$$

If we limit the expansion to the term linear in h_1 we recover the usual tanh-like profile $(\rho_l + \rho_g)/2 + \tanh(z - z_0)(\rho_l - \rho_g)/2$. Concerning the two body correlation function, since we limit the effective Hamiltonian to a ϕ^4 model, the bulk field correlation function is the same in the two phases and as a result of equation (34) this is also the case for the density correlation function $G_\rho^{(2)T}(1, 2)$. This is of course a drawback of the simplicity of the present model for the description of the liquid vapor interface. To overcome this drawback, we may have to consider a true inhomogeneous reference fluid, which imposes to chose two different values for the hard sphere reference chemical potential, ν_0 . This is beyond the scope of the present work.

5. Conclusion

We have shown in this article that the one-loop approximation of the KSSHE statistical field theory of simple liquids gives a coherent and qualitatively exact description of a planar liquid/vapor interface. The mathematical treatment of the kink is subtle and requires to take into account the whole spectrum of eigenvalues and eigenstates of the Gaussian Hamiltonian and not, as often and incorrectly proposed in the literature, to restrict oneself to its fundamental state. Moreover, without invoking any phenomenological description of the interface, we were able to recover the usual CWT surface Hamiltonian as an approximation of the one-loop calculation. 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. On the other hand, we clearly control the limit of the model by computing the two-body density correlation functions which appear to coincide in the liquid and vapor bulk phases, a drawback due to the identity of the two phases in the field ϕ representation.

Nevertheless, qualitatively, our results are in good agreement with numerical simulations. We stress that no parameter is involved in the theory which can be worked out for any pair potential. A quantitative agreement is expected only for long range pair potentials which we plan to investigate by numerical simulations in future work.

A. KSSHE Transform

In this appendix we review the so-called Kac-Siegert-Stratonovich-Hubbard-Edwards (KSSHE) [17–22] transformation devised to rewrite the GCPF of a classical fluid as the partition function of a bosonic statistical field theory; more details are given in refs [23–25].

We consider the case of a simple three dimensional fluid made of identical hard spheres of diameter σ with additional isotropic pair interactions $v(r_{ij})$ ($r_{ij} = \|x_i - x_j\|$, x_i position of particle “ i ”). Since $v(r)$ is arbitrary in the core, i.e. for $r \leq \sigma$, we assume that $v(r)$ has been regularized in such a way that its Fourier transform $\tilde{v}(q)$ is a well behaved function of q and that $v(0)$ is a finite quantity. We denote by $\Omega \subset \mathbb{R}^3$ the domain of volume V occupied by the molecules of the fluid. The fluid is at equilibrium in the GC ensemble and we denote by $\beta = 1/kT$ the inverse temperature (k Boltzmann constant) and by μ the chemical potential. For the sake of generality the particles are subject to an external potential $\psi(x)$ and $\nu(x) = \beta(\mu - \psi(x))$ is the dimensionless local chemical potential. We stick to notations usually adopted in standard textbooks on the theory of liquids (see e.g. ([43])) and denote by $w(r) = -\beta v(r)$ the negative of the dimensionless pair interaction. Moreover, we restrict ourselves to attractive interactions, i.e. such that their Fourier transform $\tilde{w}(q) > 0$ is definite positive for all q .

In a given configuration $\mathcal{C} = (N; x_1 \dots x_N)$ of the GC ensemble the microscopic density of particles reads

$$\widehat{\rho}(x|\mathcal{C}) = \sum_{i=1}^N \delta^{(3)}(x - x_i), \quad (\text{A-1})$$

and the GC partition function $\Xi[\nu]$ can thus be written as

$$\Xi[\nu] = \sum_{N=0}^{\infty} \frac{1}{N!} \int_{\Omega} d1 \dots dn \exp \left(-\beta V_{\text{HS}}(\mathcal{C}) + \frac{1}{2} \widehat{\rho} \cdot w \cdot \widehat{\rho} + \overline{\nu} \cdot \widehat{\rho} \right), \quad (\text{A-2})$$

where $\rho \cdot w \cdot \rho$ is a short hand notation for $\int \rho(1)w(1,2)\rho(2)d1d2$, $i \equiv x_i$ and $di \equiv d^3x_i$. For a given volume V , $\Xi[\nu]$ is a function of β and a convex functional of the local chemical potential $\nu(x)$ [44, 45]. In equation (A-2) $\exp(-\beta V_{\text{HS}}(\mathcal{C}))$ denotes the hard sphere contribution to the Boltzmann factor in a configuration \mathcal{C} and $\overline{\nu} = \nu + \nu_S$ where $\nu_S = -w(0)/2$ is β times the self-energy of particles. From our hypothesis on $w(r)$, ν_S is a finite quantity which depends, however, on the regularization of the potential in the core.

We now recognize the Gaussian integral [46, 47]

$$\exp \left(\frac{1}{2} \widehat{\rho} \cdot w \cdot \widehat{\rho} \right) = \frac{1}{\mathcal{N}_w} \int \mathcal{D}\varphi \exp \left(-\frac{1}{2} \varphi \cdot w^{-1} \cdot \varphi + \widehat{\rho} \cdot \varphi \right), \quad (\text{A-3})$$

where φ is a real scalar field, $\mathcal{D}\varphi$ is a functional measure, $w^{-1}(1,2)$ is the inverse of $w(1,2)$ in the sense of operators and the normalization \mathcal{N}_w reads as

$$\mathcal{N}_w = \int \mathcal{D}\varphi \exp \left(-\frac{1}{2} \varphi \cdot w^{-1} \cdot \varphi \right) = \exp \left(-\frac{V}{2} \int \frac{d^3k}{(2\pi)^3} \ln \tilde{w}(k) \right). \quad (\text{A-4})$$

It follows that the GCPF $\Xi[\nu]$ can be re-expressed as the functional integral

$$\Xi[\nu] = \mathcal{N}_w^{-1} \int \mathcal{D}\varphi \exp(-H[\varphi, \nu]), \quad (\text{A-5})$$

where the KSSHE action (or effective Hamiltonian) is expressed as

$$H[\varphi, \nu] = \frac{1}{2} \varphi \cdot w^{-1} \cdot \varphi - \ln \{ \Xi_{\text{HS}}[\overline{\nu} + \varphi] \}. \quad (\text{A-6})$$

The action $H[\varphi, \nu]$ is non-canonical in the sense that the coupling between the field φ and the external source $\overline{\nu}$ is non-linear as in usual Landau-Ginzburg actions [47]. In order to get a canonical field theory we perform the translation $\phi = \varphi + \Delta\nu$ with $\Delta\nu = \overline{\nu} - \nu_0$ where ν_0 is some arbitrary uniform reference chemical potential to be conveniently chosen later. The Jacobian of the transformation is obviously equal to one and then, performing a Taylor functional expansion of the grand potential $\ln \{ \Xi_{\text{HS}}[\nu_0 + \phi] \}$ about ν_0 we obtain a standard scalar field theory [23–25], characterized by the partition function

$$\Xi^*[B] = \mathcal{N}_w^{-1} \int \mathcal{D}\phi \exp \left(\frac{1}{2} \phi \cdot \Delta^{-1} \cdot \phi - V[\phi] + B \cdot \phi \right), \quad (\text{A-7})$$

where the propagator $\Delta(x, y)$ and the interaction $V[\phi]$ are given by

$$\Delta^{-1}(x, y) = w^{-1}(x, y) + G_{\text{HS}}^{(2)\text{T}}(\nu_0|x, y), \quad (\text{A-8a})$$

$$V[\phi] = - \sum_{n=3}^{\infty} \frac{1}{n!} \int dx_1 \dots dx_n G_{\text{HS}}^{(n)\text{T}}(\nu_0|x_1, \dots, x_n) \phi(x_1) \dots \phi(x_n), \quad (\text{A-8b})$$

where the $G_{\text{HS}}^{(n)\text{T}}$ are the truncated n-body correlation functions of a HS fluid at chemical potential ν_0 [43]

$$G_{\text{HS}}^{(n)\text{T}}(\nu_0|x_1, \dots, x_n) = \frac{\delta^n \ln \Xi_{\text{HS}}[\nu_0]}{\delta\nu_0(x_1) \dots \delta\nu_0(x_n)}, \quad (\text{A-9})$$

which are supposed to be exactly known, and where, finally, the external source or “magnetic” field $B(x)$ of the theory is related to the local chemical potential through the linear relation

$$B(x) = \rho_{\text{HS}}(\nu_0) + w^{-1}(x, y)\Delta\nu(y), \quad (\text{A-10})$$

where Einstein convention of summation over repeated indices – here continuous variable y – was adopted. The free energies of the non-canonical and canonical theories differ essentially by a quadratic form, i.e.

$$\ln \Xi[\nu] = \ln \Xi_{\text{HS}}[\nu_0] - \frac{1}{2}\Delta\nu \cdot w^{-1} \cdot \Delta\nu + \ln \Xi^*[B], \quad (\text{A-11})$$

which allows us to easily relate the correlations of the density to that of the field. With the definitions

$$G_\rho^{(n)\text{T}}(\nu|x_1, \dots, x_n) = \frac{\delta^n \ln \Xi[\nu]}{\delta\nu(x_1) \dots \delta\nu(x_n)}, \quad (\text{A-12a})$$

$$G_\phi^{(n)\text{T}}(B|x_1, \dots, x_n) = \frac{\delta^n \ln \Xi^*[B]}{\delta B(x_1) \dots \delta B(x_n)}, \quad (\text{A-12b})$$

one finds [23–25]

$$\rho(x) = w^{-1}(x, y) \{ \langle \phi \rangle(y) - \Delta\nu(y) \} = w^{-1}(x, y) \langle \varphi \rangle(y), \quad (\text{A-13a})$$

$$G_\rho^{(2)\text{T}}(x, y) = -w^{-1}(x, y) + w^{-1}(x, x')w^{-1}(y, y')G_\phi^{(2)\text{T}}(x', y'), \quad (\text{A-13b})$$

$$G_\rho^{(n)\text{T}}(x_1, \dots, x_n) = w^{-1}(x_1, x'_1) \dots w^{-n}(x_1, x'_n)G_\phi^{(n)\text{T}}(x'_1, \dots, x'_n) \quad \text{for } n \geq 3. \quad (\text{A-13c})$$

Note that the *truncated* n-body correlation functions of the fields ϕ and φ coincide for $n \geq 2$ since the two fields differ by a simple additional function.

At this point we introduce some approximations. First we adopt the “point of view of Sirius” and consider the kernels $G_{\text{HS}}^{(n)\text{T}}(\nu_0|x_1, \dots, x_n)$ to be short-range functions of their arguments when compared with the range of variations of field or density correlations near the critical point. More precisely, we assume that, for $n \geq 3$, one has

$$G_{\text{HS}}^{(n)\text{T}}(\nu_0|x_1, \dots, x_n) \approx \beta P_{\text{HS}}^{(n)}(\nu_0)\delta(x_n, x_1) \dots \delta(x_2, x_1), \quad (\text{A-14})$$

where $P_{\text{HS}}^{(n)}(\nu_0)$ denotes the n-th derivative of the HS pressure with respect to the chemical potential ν_0 . Moreover, neglecting high-order contributions to $V[\phi]$ we get the somehow sketchy interaction

$$V[\phi] \approx \frac{u_3}{3!} \int dx \phi^3(x) + \frac{u_4}{4!} \int dx \phi^4(x), \quad (\text{A-15})$$

where $u_n = -\beta P_{\text{HS}}^{(n)}(\nu_0) = -\rho_{\text{HS}}^{(n-1)}(\nu_0)$, which should be valid but very close to the critical point. Note that one should have $u_4 > 0$ for the action to be bounded from below at large fields so that the theory is well-behaved.

A similar approximation is devised for the propagator for which we adopt a gradient expansion up to the second order, more conveniently written in Fourier space as

$$\tilde{\Delta}^{-1}(q_1, q_2) = (2\pi)^3 \delta^{(3)}(q_1 + q_2) \tilde{\Delta}^{-1}(q_1), \quad (\text{A-16a})$$

$$\tilde{\Delta}^{-1}(q) = \tilde{w}^{-1}(q) + \tilde{\mathcal{C}}_{\text{HS}}^{(2)}(q) = K_0 + K_2 q^2 + \mathcal{O}(q^4), \quad (\text{A-16b})$$

where the Ornstein-Zernicke relation $\tilde{\mathcal{C}}_{\text{HS}}^{(2)}(q) = -1/\tilde{G}_{\text{HS}}^{(2)\text{T}}(q)$ defines the Fourier transform of the HS two-body direct correlation function (the definition of which includes an ideal gas contributions so that $\tilde{\mathcal{C}}_{\text{HS}}^{(2)}(q) = \tilde{c}_{\text{HS}}(q) - 1/\rho$, $\tilde{c}_{\text{HS}}(q)$ being a usual direct correlation function [43].) A short calculation gives

$$K_0 = \frac{1}{\tilde{w}(0)} - \rho_{\text{HS}}^{(1)}(\nu_0), \quad (\text{A-17a})$$

$$K_2 = \frac{1}{2} \left\{ -\frac{\tilde{w}_2}{\tilde{w}(0)^2} + \tilde{c}_{\text{HS},2} \rho_{\text{HS}}^{(1)}(\nu_0)^2 \right\}, \quad (\text{A-17b})$$

where \tilde{w}_2 and $\tilde{c}_{\text{HS},2}$ are the second derivatives of $\tilde{w}(q)$ and $\tilde{c}_{\text{HS}}(q)$ with respect to q at $q = 0$, respectively. The quantities entering the coupling constants K_0 and K_2 in equations (A-17) require the knowledge of the equation of state and pair correlation functions of the HS fluid, which can be done in the framework of Percus-Yevick theory, for instance [43].

At this point we choose ν_0 such that $u_3 = -\rho_{\text{HS}}''(\nu_0) = 0$ so that the action \mathcal{S} of field ϕ reduces exactly to that of a ϕ^4 Landau-Ginzburg model, i.e.

$$\mathcal{S} = -\phi \cdot B + \int dx \left\{ \frac{1}{2} K_0 (\nabla \phi)^2 + \frac{1}{2} K_2 \phi^2 + \frac{u_4}{4!} \phi^4 \right\}. \quad (\text{A-18})$$

A last remark is in order. As discussed in [25] the chemical potential $\nu_0 \approx -0.025$ is uniquely defined (a consequence of the expected – and satisfied – convexity of the function $\nu \mapsto \rho'_{\text{HS}}(\nu)$) and such that $\rho_{\text{HS}}(\nu_0) \approx 0.25$, $\rho_{\text{HS}}^{(1)}(\nu_0) \approx 0.09$ and $u_4 > 0$.

References

1. Sullivan D.E., Telo da Gamma M.M., Fluid Interfacial Phenomena. CA Croxton ed., Wiley, 1986, p. 45.
2. Forgacs G., Lipowsky R., Nieuwenhuizen T., Phase Transitions and Critical Phenomena, Academic Press, 1991, **14**, 135.
3. Dietrich S., Phase Transitions and Critical Phenomena, Academic Press, 1988, **12**, 1.
4. Lipowsky R., Kroll D.M., Zia R.K.P., Phys. Rev. B, 1982, **32**, 1862.
5. Brézin E., Halperin B.H., Leibler S., J. Physique, 1983, **44**, 775.
6. Parry A.O., Swain P.S., Physica A, 1998, **250**, 167.
7. Orlandi A., Parola A., Reatto L., Phys. Rev. E, 2004, **70**, 051611.
8. Buff F.P., Lovett R.A., Stillinger F.H., Phys. Rev. Lett., 1965, **15**, 621.
9. Fisher D.S., Huse Ph D.A., Phys. Rev. B, 1985, **32**, 247.
10. Parry A.O., Boulter C.J., J. Phys.: Condens. Matter, 1994, **6**, 7199.
11. Brilliantov N.V., Rubi J.M. Preprint arXiv: cond-mat/0210340.
12. Romero-Rochín V., Varea C., Robledo A., Physica A, 1992, **184**, 367.
13. Dietrich S., Napiorkowski M., Physica A, 1991, **177**, 437.
14. Mecke K.E., Dietrich S., Phys. Rev. E, 1999, **59**, 6766.
15. Blokhuis E.M., J. Chem. Phys., 2009, **130**, 014706.
16. Russier V., Caillol J.-M., J. Physical Studies, 2009, in press (work presented at the “Statphys’09” conference in Lviv, Ukraine); Preprint arXiv:0907.2808v1 [cond-mat.stat-mech].
17. Kac M., Phys. Fluids., 1959, **2**, 8.
18. Siegert A.J.F., Physica, 1960, **26**, S30.
19. Stratonovich R.L., Sov. Phys. Solid State, 1958, **2**, 1824.
20. Hubbard J., Phys. Rev. Lett., 1954, **3**, 77.
21. Hubbard J., Shofield P., Phys. Lett. A, 1972, **40**, 245.
22. Edwards S.F., Phil. Mag. B, 1959, **4**, 1171.
23. Caillol J.-M., Patsahan O., Mryglod I., Physica A, 2006, **368**, 326.
24. Caillol J.-M., Patsahan O., Mryglod I., J. Phys.: Condens. Matter, 2005, **8**, 665.
25. Caillol J.-M., Mol. Phys., 2003, **101**, 1617.
26. Lipowsky R., Fisher M.E., Phys. Rev. B, 1987, **36**, 2126.
27. Fisher M.E., Jin A.J., Phys. Rev. B, 1991, **44**, 1430.
28. Chaikin P.M., Lubensky T.C. Principles of Condensed Matter Physics. Cambridge University Press, Cambridge, 1995, chap. 10.
29. Brilliantov N.V., Phys. Rev. E, 1998, **58**, 2628.
30. Zittartz J., Phys. Rev., 1967, **154**, 529.
31. Infeld L., Hull T.E., Rev. Mod. Phys., 1951, **23**, 21.
32. Evans R., Mol. Phys., 1981, **42**, 1169.
33. Di Caprio D., Stafiej J., Badiali J.-P., Electrochim. Acta, 2003, **48**, 2967.
34. Binney J.J., Dowrick N.J., Fisher A.J., Newman M.E.J., An Introduction to the Renormalization Group. Oxford University Press, Oxford, 1992.
35. Boulter C.J., Mod. Phys. Lett. B, 2001, **15**, 993.
36. Zia R.K.P., Nucl. Phys. B, 1984, **251**, 676.

37. Diehl H.W., Zia R.K.P., Phys. Rev. Lett., 2001, **87**, 209601.
38. Segovia-López J.G., Romero-Rochín V., Phys. Rev. Lett., 2001, **86**, 2369.
39. Vink R.L.C., Horbach J., Binder K., J. Chem. Phys., 2005, **122**, 134905.
40. Sedlmeier F., Horinek D., Netz R., Phys. Rev. Lett., 2009, **103**, 130602.
41. Chacon E., Tarazona P., Phys. Rev. Lett., 2003, **91**, 166103.
42. Tarazona P., Checa R., Chacón E., Phys. Rev. Lett., 2007, **99**, 196101.
43. Hansen J.P., Mc Donald I.R., Theory of Simple Liquids. Academic Press, London, 1986.
44. Goldenfeld N., Lectures on Phase Transitions and the Renormalization Group. Addison-Wesley, 1992.
45. Caillol J.-M., J. Phys. A, 2002, **35**, 4189.
46. Wegner F., Phase Transitions and Critical Phenomena **6**. Academic Press, New-York, 1976.
47. Zinn-Justin J., Quantum Field Theory and Critical Phenomena. Clarendon Press, London, 1989.

Статистико-польова теорія міжфазної границі рідина-пара

В. Русьєр¹, Ж.-М. Кайоль²

¹ Інститут хімії і матеріалів, UMR 7182 CNRS і Університет Парі-ЕСТ, Франція

² Лабораторія теоретичної фізики, UMR 8627 CNRS і Університет Парі-Сюд, Франція

З перших принципів розвинуто статистико-польову теорію для неоднорідної рідини, плоскої міжфазної границі рідина/пара. Велика статистична сума представляється через перетворення Габбарда-Стратоновича, що приводить поблизу критичної точки до звичної скалярної теорії поля ϕ^4 , яка потім строго розглядається на однопетльовому рівні. Після подальшого спрощення це дає добре відому теорію капілярної хвилі без жодного *ad hoc* феноменологічного параметра. Обговорюється внутрішня узгодженість однопетльового наближення і наголошується на доброму якісному узгодженні з недавніми числовими симуляціями.

Ключові слова: теорія поля, міжфазна границя газ-рідина, поверхневий натяг
