Surface tension of liquids near the critical point

N.V. Brilliantov\textsuperscript{1,2} and J.M. Rubi\textsuperscript{1}

\textsuperscript{1}Departament de Fisika Fonamental, Universitat de Barcelona, Av.Diagonal 617, 08028 Barcelona, Spain and
\textsuperscript{2}Moscow State University, Physics Department, Moscow 119899, Russia

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A simple analytical microscopic expression for the surface tension of liquids $\gamma$ is obtained which is in a good agreement with available data of numerical experiments. We apply the integral transformation that maps the fluid Hamiltonian onto the field-theoretical Hamiltonian and show that the order parameter of the effective Hamiltonian corresponds to the one-body potential in the fluid. Revealing the physical meaning of the order parameter allows calculation of $\gamma$.

The modern theory of nonuniform fluids is based mainly on the integral equations hierarchy or density functional theory \cite{1}. Recent applications of the latter theory to the problems of interface formation and surface tension demonstrated its accuracy and effectiveness \cite{2,3}. Although the density functional theory often uses \textit{ad hoc} approximations, rather than regular expansion schemes \cite{4,5}, it is essentially the first-principle theory: No model parameter are involved, and for a given interparticle potential, temperature, etc., the density distribution model parameter are involved, and for a given interparticle potential is postulated. For the most frequently used square-gradient model it reads (e.g. \cite{5,6})

$\beta H = \int d\mathbf{r} \left[ (\kappa/2)(\nabla \phi)^2 + V(\phi) \right]$ \hspace{1cm} (1)

where the first term accounts for the free energy penalty due to inhomogenity and $V(\phi)$ is chosen to mimic a possibility of the two-phase coexistence. Its simplest choice corresponds to the Landau-Ginzburg-Wilson (LGW) Hamiltonian:

$V(\phi) = (a_2/2)\phi^2(\mathbf{r}) + (a_4/4!)\phi^4(\mathbf{r}) - h(\mathbf{r})\phi(\mathbf{r}),$ \hspace{1cm} (2)

with the free energy, $-\beta F = \log \int D\phi \exp(-\beta H)$ ($\beta = 1/k_BT$), which accounts for all possible distributions of the order parameter, and not only for the extremal one, as in the density functional theory. The powerful field-theoretical methods, elaborated especially for the LGW Hamiltonian \cite{5,6} may be then applied to describe the critical fluctuations, and a simple analytical expression for the surface tension may be derived \cite{4,7}.

The order parameter $\phi(\mathbf{r})$ in \cite{4,7} may be of any physical nature, (density, composition of the fluid mixture \cite{7}, magnetization \cite{6}, etc.), while the coefficients of the Hamiltonian $H$ are some model parameters for which microscopic expressions are not provided. Therefore the field theoretical approach is not now, strictly speaking, a microscopic theory.

The present study is addressed to overcome this flaw. We obtain an effective field theoretical Hamiltonian for the fluid with microscopic expressions for its coefficients. We show that the order parameter of this Hamiltonian corresponds to the one-body microscopic potential, and its average to the first-order direct correlation function.

Revealing the physical nature of the order parameter we obtain an analytical expression for the surface tension which is in a good agreement with numerical experiments.

Referring for detail to \cite{4,7} we briefly sketch derivation of the effective LGW Hamiltonian, which is similar to that of Hubbard and Schofield \cite{10}. We start from the fluid Hamiltonian $H = H_R + H_A + H_{ex}$:

$$H = \sum_{i<j} v_{ij}(\mathbf{r}_{ij}) - \sum_{i<j} v(\mathbf{r}_{ij}) + \sum_j g(\mathbf{r}_j)$$ \hspace{1cm} (3)

where $v_{ij}(\mathbf{r})$ denotes the repulsive part of the interaction potential, $-v(\mathbf{r})$ denotes the attractive part and $g(\mathbf{r})$ denotes the external potential; $\{\mathbf{r}_j\}$ are coordinates of the particles and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The last two terms of the fluid Hamiltonian \cite{4} may be written using the Fourier transforms of the density fluctuations, $n_k = (1/\sqrt{\Omega}) \sum_{l=1}^N e^{-ik\cdot\mathbf{r}_l}$, of the attractive potential, $v_k = \int v(\mathbf{r}) e^{-ik\cdot\mathbf{r}} d\mathbf{r}$ and of the external potential $g_k = \int g(\mathbf{r}) e^{-ik\cdot\mathbf{r}} d\mathbf{r}$ as

$$-\left(1/2\right) \sum_k v_k n_k n_{-k} + (1/2) v(0) N + \sum_k g_k n_{-k},$$ \hspace{1cm} (4)

where $N$ is the number of particles, $\Omega = L^3$ is the volume of the system ($L \to \infty$), and summation over $k_l = \frac{2\pi}{L} n_l$ with $l = x, y, z$, and $n_l = 0, \pm 1, \ldots$ is implied. Let $\mu$...
be the chemical potential of the system with the “complete” Hamiltonian, \( \delta \), and \( \mu_R \) be the chemical potential of the “reference” system, with the Hamiltonian, \( H_R \), which has only repulsive interactions. Then the grand partition function, \( \Xi \), may be expressed in terms of the grand partition function, \( \Xi_R \) of the reference fluid as

\[
\Xi = \Xi_R \left\{ \exp \left\{ \beta \mu' N + \beta \sum_k \left[ \frac{\nu_k}{2} n_k n_{-k} - n_k g_{-k} \right] \right\} \right\}_R,
\]

where \( \mu' = \mu - \mu_R + \frac{1}{T} v(0) \) and \( \langle \rangle_R \) denotes an average over the reference system at temperature \( T \) with chemical potential \( \mu_R \). Using the identity: \( \exp(\frac{1}{2} a^2 x^2 - bx) = (2\pi a^2)^{-1/2} \int_0^{\infty} \exp[-\frac{1}{2}(y + b)^2/a^2 + xy] dy \), we obtain for the ratio \( Q = \Xi / \Xi_R \):

\[
Q \propto \int \prod_k d\phi_k \left\{ \exp \left\{ \sum_k \phi_k n_{-k} \right\} \right\}_R \exp \left\{ \frac{\mu'}{\nu_0} \Omega^{1/2} \phi_0 \right\} - \frac{1}{2} \beta^{-1} \sum_k v_k^{-1} (\phi_k + \beta g_k) (\phi_k + \beta g_{-k}) \right\} ;
\]

(6)

here integration is to be performed under the constrain \( \phi_{-k} = \phi_k^* \) and a factor which does not affect the subsequent analysis is omitted. Applying the cumulant theorem to the factor \( \langle \exp \{ \sum_k \phi_k n_{-k} \} \rangle_R \) one can write

\[
Q \propto \int \prod_k d\phi_k \exp(-\beta H) \]

(7)

\[
\beta H = -\hbar \Omega^{1/2} \phi_0 + \sum_{n=2}^{\infty} \Omega^{1-n/2} \sum_{k_1, \ldots, k_n} \tilde{u}_n \phi_{k_1} \cdots \phi_{k_n} ,
\]

where the coefficients of the effective field theoretical Hamiltonian \( H \) read for \( g(\mathbf{r}) = 0 \): \( h = \mu' \nu_0^{-1} + \rho \), and

\[
\tilde{u}_2 (k_1, k_2) = (1/2! \} \delta_{k_1+k_2,0} \left\{ \beta^{-1} v_{k_1}^{-1} - \langle n_{k_1} n_{-k_1} \rangle \right\} ,
\]

\[
\tilde{u}_n (k_1, \ldots, k_n) = -\langle \Omega^{n-2/1}/n! \rangle \langle n_{k_1} \cdots n_{k_n} \rangle \}
\]

(8)

for \( n \geq 3 \). Here \( \langle \rangle_{\theta R} \) denotes the cumulant average calculated in the (homogeneous) reference system and \( \rho = \Omega^{-1/2} \sigma \sigma_R = N / \Omega \) is the fluid density. According to \( 9 \), \( Q \) has the form of a partition function.

As it follows from \( 9 \) the coefficients of \( H \) depend on correlation function of the reference fluid having only repulsive interactions. Using definitions of the particle correlation functions of fluids \( 11 \), one can express the cumulant averages \( \langle n_{k_1} \cdots n_{k_n} \rangle_{\theta R} \) and thus the coefficients \( \tilde{u}_n (k_1, \ldots, k_n) \) in terms of the Fourier transforms of the connected correlation functions \( h_1, h_2, \ldots, h_n \) of the reference system. These are defined as \( h_1 (\mathbf{r}_1) \equiv \delta (\mathbf{r}_1) \), \( h_2 (\mathbf{r}_1, \mathbf{r}_2) \equiv g_2 (\mathbf{r}_1, \mathbf{r}_2) - 1 \), \( h_3 (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g_3 (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2 (\mathbf{r}_1, \mathbf{r}_2) - g_2 (\mathbf{r}_1, \mathbf{r}_3) - g_2 (\mathbf{r}_2, \mathbf{r}_3) + 2 \), etc., where \( g_l (\mathbf{r}_1, \ldots, \mathbf{r}_l) \) are \( l \)-particle correlation functions \( 11 \). In particular, the first few coefficients read \( 8 \)

\[
\tilde{u}_2 = (1/2! \} \left[ \beta v_0 \right] - \rho^2 \tilde{h}_2 (k_1, k_2) \}
\]

\[
\tilde{u}_3 = -(1/3!) \left\{ \rho + \rho^2 \left[ \tilde{h}_2 (k_1) + \tilde{h}_2 (k_2) + \tilde{h}_2 (k_3) \right] \}
\]

\[
\right\} \delta_{k_1+k_2+k_3,0} ;
\]

(9)

(10)

where \( h_l \) are the Fourier transforms of \( h_l \).

To obtain the conventional square gradient form of the effective Hamiltonian we perform the small-\( k \) expansion of the coefficients \( \tilde{u}_n (k_1, \ldots, k_n) \). From the structure of the LGW Hamiltonian \( 8 \), which has the only gradient term \( \nabla^2 \phi_0 \sim k^2 \phi_0 \phi_{-k} \), follows that only \( \tilde{u}_2 \) should be expanded as \( \tilde{u}_2 = \tilde{u}_2 (0) - \tilde{u}_2 (0)^\prime k^2 + \cdots \), while the other coefficients \( \tilde{u}_n \), \( n \geq 3 \) should be taken at zero wavevectors, as \( \tilde{u}_n (0, 0, \ldots, 0) \) \( 8 \). Thus, as it is seen from \( 8 \) only \( h_2 (0), h_2 (0)^\prime \) and \( h_l (0) \) \( l=1,0, \ldots \), \( l \geq 2 \), are needed. To find the latter we use the chain relation for the successive correlation functions \( 8 \)

\[
\rho_0 \frac{d}{d\rho} \rho \tilde{h}_l (0) = \rho \left[ \tilde{l} \tilde{h}_l (0) + \tilde{h}_{l+1} (0) \right]
\]

(11)

expressing each \( \tilde{h}_{l+1} (0) \) in terms of \( \tilde{h}_l (0) \) and its density derivative. Here \( z_0 \equiv \beta^{-1} \left( \partial P/\partial \rho \right)^{\gamma} \) is the reduced isothermal compressibility and \( P \) is the pressure. With \( h_l (0) = 1 \), Eq. \( 11 \) allows to express iteratively each of \( \tilde{h}_l (0) \), (which refer to the reference fluid) in terms of the reduced compressibility of the reference fluid \( z_0 \) and its density derivatives \( \partial z_0 / \partial \rho, \partial^2 z_0 / \partial \rho^2 \), etc.

For the reference system with the only repulsive interactions one can use the hard-sphere system with an appropriately chosen diameter \( 11 \). For soft (not impulsive) repulsive forces a simple relation \( 11 \) \( d = \int d^3 r \left\{ 1 - \exp(-\beta v_r (r)) \right\} \) gives the effective diameter of the hard-sphere system, corresponding to a repulsive potential \( v_r (r) \) vanishing at \( r \geq \sigma \). The fairly accurate Carnahan-Starling equation of state for this system \( 11 \) yields for the reduced compressibility

\[
z_0 = (1 - \eta^4) / (1 + 4 \eta + 4 \eta^2 - 4 \eta^3 + \eta^4)
\]

(12)

where \( \eta = \frac{4}{\pi} d^3 \rho \). For the hard-sphere reference system one can also find \( \tilde{h}_2 (0)^\prime \). This may be done expressing \( \tilde{h}_2 (k) \) in terms of the direct correlation function \( \tilde{c}_2 (k) \), as \( h_2 (k) = \tilde{c}_2 (k) \) \( 11 \), expanding \( \tilde{c}_2 (k) \) as \( \tilde{c}_2 (k) = \tilde{c}_2 (0) - \tilde{c}_2 (0)^\prime k^2 + \cdots \) and using \( \tilde{c}_2 (0)^\prime = -\left( \pi d^3 /120 \right) (16 - 11 \eta + 4 \eta^2) (1 - \eta^4) \) which may be obtained from the Wertheim-Thiele solution \( 11 \) for the direct correlation function \( 8 \).

Following these lines we find explicit expressions for all coefficients of the effective Hamiltonian \( 8 \). To recast this into conventional form \( 11 \) we (i) perform transformation from variables \( \phi_k \) to the space-dependent field
where $\rho$ is the one-particle density, and $\mu$ is the chemical potential. Not far from the critical point, the density of the field $\phi$ at $x \to -\infty$, and $\phi^*_2$ at $x \to \infty$, are related to the mean densities of these phases: the liquid, $\rho_l$, and the vapor, $\rho_g$ density. Using the fact that in the bulk $\phi^*_1, 2 = \beta v_0 \rho_l, g + \phi$, one can show that $\phi^*_1$ and $\phi^*_2$ may be obtained by the standard double-tangent construction, $V'(\phi^*_1) = V'(\phi^*_2)$ and $V(\phi^*_1) + \phi^*_1 V'(\phi^*_1) = V'(\phi^*_2) + \phi^*_2 V'(\phi^*_2)$. If we choose interface located at $x = 0$, (16) yields $\frac{\kappa d\phi^*/dx^2}{dx} = V(\phi^*) - V(\phi^*_1)$ for $x < 0$ and $\frac{\kappa d\phi^*/dx^2}{dx} = V(\phi^*) - V(\phi^*_2)$ for $x > 0$. The surface tension is equal to the difference per unit area between the free energy, calculated for the space-dependent $\phi^*(r)$ and that for $\phi^*_1$ for $x < 0$ and $\phi^*_2$ for $x > 0$. If the order parameter at the interface equals $\phi^*_1$, which may be chosen from the condition $\phi^*_1 < \phi^*_0 < \phi^*_2$, $V'(\phi^*_0) = 0$ the surface tension reads (with $V_{1,2} = V(\phi^*_{1,2})$):

$$\beta \gamma = \int_{\phi^*_1}^{\phi^*_2} \sqrt{2\kappa[V(\phi) - V_1]} d\phi + \int_{\phi^*_1}^{\phi^*_2} \sqrt{2\kappa[V(\phi) - V_2]} d\phi$$

Now we choose the system for which the coefficient $h$ in (13) vanishes, i.e. $h = 0$. Then for $V = \frac{1}{2} \phi^2 + \frac{1}{4} u_4 \phi^4$ we obtain $\phi^*_1, 2 = \pm \frac{1}{2} \beta v_0 u_4^{1/2}$, and thus using solution to Eq. (15), $\phi^* = (-6a_2 u_4)^{1/2} \tanh(x/\xi_0)$, with zero over the volume average, $\phi^* = \Omega^{-1} \int \phi^*(r) dr = 0$.

Averaging over the volume (15), yields $\phi^* = \beta \rho_l + \phi$, which implies that $\phi = \phi^* + \phi_l$, with $\rho = \Omega^{-1} \int \rho(r) dr = N/\Omega$ being the averaged over the volume density. Since $\phi^*_1 = -\phi^*_2$ and simultaneously $\phi^*_1, 2 = \pm \beta v_0 \rho_l + \phi$, we finally conclude that $\rho = (\rho_l + \rho_g)/2$, i.e. that the averaged density of our system is the mean between the liquid and vapor density. Naturally, this is the density of our homogeneous reference system, which has the same volume and number of particles. With the above $\phi^*_1, 2$ and $\phi^*_0$, integration in (17) is easily performed yielding:

$$\gamma/k_B T = \frac{4}{\kappa} \frac{(2 \kappa a_2^2 / u_4^2)^{1/2}}{u_4}$$

where microscopic expressions for the constants $a_2$, $u_4$, $\kappa$, are given by Eqs.(13-14) in which the density $\rho = (\rho_l + \rho_g)/2$ of the reference fluid is to be used.

Not far from the critical point $(\rho_c, T_c)$, one can approximate, $(\rho_l + \rho_g)/2 \approx \rho_c$, and thus use $\rho_c$ as the reference density. In particular one can write for $a_2: a_2 \approx \approx 2(\beta, \rho_c = (\beta v_0)^{-1} - \rho_c(2z_0^2/2 u_4) \epsilon$ (see (15)). If we then use the mean field condition for the critical
point, \( a_2(\beta_c, \rho_c) = 0 \), we obtain a simple expression:
\[
a_2 = (\beta v_0)^{-1} - (\beta_c v_0)^{-1} = \alpha \tau,
\]
and finally for the surface tension:
\[
\gamma/k_B T = 4 \left( 2 \kappa_c \alpha^3 / u_{4c}^2 \right)^{1/2} \tau^{3/2},
\]
where \( \alpha = (\beta_c v_0)^{-1} \), \( \tau = (T_c - T)/T_c \), and coefficients \( u_{4c} \) and \( \kappa_c \) are to be calculated at \( \rho = \rho_c, T = T_c \).

\[\begin{align*}
\gamma/k_B T & = 4 \left( 2 \kappa_c \alpha^3 / u_{4c}^2 \right)^{1/2} \tau^{3/2}, \\
\end{align*}\]

In conclusion, we derive an analytical microscopic expression for the surface tension which allows (for the first time to our knowledge) to obtain this quantity for the given temperature, density and interaction potential. This relation is in a good agreement with numerical experiments in the near-critical region. Our theory is based on the effective field theoretical Hamiltonian, which order parameter corresponds to the microscopic one-body potential and its average to the first-order direct correlation function. Although our mean field result is not valid in the very close vicinity of the critical point, its generalization to account the critical fluctuations (e.g. within the one-loop approximation) is straightforward, and will be addressed elsewhere.

The theoretical expression for the surface tension (19) has been compared with available data of numerical experiments for the Lennard-Jones (LJ) and hard-core Yukawa (HCY) fluids, for which the standard WCA partition (see e.g. [1]) of the potential into attractive and repulsive parts has been applied [8]. As follows from Fig.1 our theory is in a good agreement with the numerical experiments, except for the very close vicinity of the critical point, where the mean field theory loses its accuracy. Eq.(19) is quite sensitive to the critical parameters \( \rho_c, T_c \). While these are known quite accurately for the LJ fluid, they are estimated with much larger uncertainty for the HCY fluid. This is shown in Fig.1 where two theoretical curves (2 and 2′) correspond to the same HCY fluid but with \( \rho_c, T_c \), taken from different references (\( \rho_c \) and \( T_c \) differ by about 4%).

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