Whether the mean–field two–length scale theory of hydrophobic effect can be microscopically approved?

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We discuss the simple microscopic derivation of a hydrophobic effect. Our approach is based on the standard functional representation of the partition function of interacting classical particles and subsequent passage to collective variables (local densities of the solvent). We get an expression for the solvation free energy of solute molecule of any arbitrary shape and derive the nonlinear equation for the mean solvent density surrounding the solvated object. We pay a special attention to some inconsistencies between the microscopic consideration and the two–length scale mean–field theory of hydrophobic effect.

I. INTRODUCTION

The key problem in thermodynamics of hydrophobic interactions consists in accounting of the effect of fluctuating media on interactions between solvated molecules. In brief, the hydrophobic effect occurs due to expelling the solvent from the volume occupied by solute molecule. Hence, the effect of solvation can be accounted by forcing the total solvent density to be zero inside the solute molecule.

Among various theoretical attempts in developing a constructive theory of solvent–solute interactions, special attention deserve the works where the hydrophobic effect is treated in the mean–field approximation with explicit separation of two characteristic length scales \([1, 2, 3]\). In this approach the fluctuating solvent density is decomposed in two components, the slowly varying field describing the mean solvent (water) density, and the short–ranged density fluctuations (usually supposed to be Gaussian) describing correlations in the solvent on scales of order of size of solvent molecules. There is a general belief that such an approach is optimal from different points of view: on one hand it is physically clear, being “semi-microscopic”, and on other hand, it can be used as a constructive computational tool of account of water, much faster than corresponding explicit approaches, but without essential loss of precision. In particular, minimization of the free energy in the frameworks of the two–length scale approach allows to determine the fluctuating solvent density is decomposed in two components, the slowly varying field describing the mean solvent (water) density, and the short–ranged density fluctuations (usually supposed to be Gaussian) describing correlations in the solvent on scales of order of size of solvent molecules. There is a general belief that such an approach is optimal from different points of view: on one hand it is physically clear, being “semi-microscopic”, and on other hand, it can be used as a constructive computational tool of account of water, much faster than corresponding explicit approaches, but without essential loss of precision. In particular, minimization of the free energy in the frameworks of the two–length scale approach allows to determine the structure of hydrophobic layer and the solvation free energy of solute molecules of any geometry, if the density–density correlation function of the pure solvent is known.

To be precise, the two–length scale approach deals with the following Hamiltonian

\[
\mathcal{H}_0[\omega, n] = \frac{1}{2} \int \omega(r) \chi^{-1}(r, r') \omega(r') d^3r + \int \left\{ \frac{a}{2} (\nabla n(r))^2 + W(n(r)) \right\} dr + c \int n(r) \omega(r) d^3r
\]

(1)

where \(n(r)\) is the smoothly changing (average) solvent density; \(\omega(r)\) is the field corresponding to the short–ranged density fluctuations; \(\chi(|r - r'|)\) is the solvent correlation function in the bulk; \(a\) is the phenomenological parameter which requires the microscopic determination—see the discussions in \([4]\); the last term describes the interaction between short– and long–scale terms with the coupling constant \(c\); and the self–consistent potential \(W(n(r))\) is chosen in the common form of the standard Ginzburg–Landau (GL) expansion for the order parameter \(n(r)\) as the fourth–order polynomial allowing the liquid–vapor phase transition:

\[
W(n) = \frac{b}{2} (n - n_1)^2 (n - n_2)^2 \quad (0 \leq n_1 \leq n_2 \leq 1)
\]

(2)

where \(n_1\) and \(n_2\) are the values of the order parameter \(n\) in the vapor and liquid phases correspondingly (below we set, if not specified, \(n_1 = 0\)) and \(b\) is the coupling constant which in combination with the parameter \(a\) defines the surface tension.

Following the general scheme of the works \([3]\), we suppose that the solvent cannot penetrate into the volume occupied by the solute molecule. Hence the total solvent density \(\rho(r) = n(r) + \omega(r)\) is nullified inside the solute: \(\rho(r) = 0\) for all \(r \in v_n\), where \(v_n\) is the volume occupied by the solute molecule. The fact that we force the total
solvent density \( \rho(\mathbf{r}) = n(\mathbf{r}) + \omega(\mathbf{r}) \) to be zero inside the solute, results in an effective interactions between \( n(\mathbf{r}) \) and \( \omega(\mathbf{r}) \). In general, one can permit also the direct coupling between \( n(\mathbf{r}) \) and \( \omega(\mathbf{r}) \) everywhere in the solute. Minimizing the corresponding free energy functional, we arrive at the set of equations for the profile of the mean solvent density \( n(\mathbf{r}) \) in presence of the solute molecule:

\[
- a \Delta n(\mathbf{r}) + \frac{\delta W(n(\mathbf{r}))}{\delta n(\mathbf{r})} + \int_{v_{in}} d\mathbf{r}' \chi_{in}^{-1}(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') = 0 \quad \text{for } \mathbf{r} \in v_{in} \tag{3a}
\]

\[
- a \Delta n(\mathbf{r}) + \frac{\delta W(n(\mathbf{r}))}{\delta n(\mathbf{r})} + U(\mathbf{r}) = 0 \quad \text{for } \mathbf{r} \in v_{out} \tag{3b}
\]

where it is supposed for simplicity that \( c = 0 \) (see (1)). We are able to compute also the corresponding solvation free energy—see [4] for details.

The theory of hydrophobic effect based on the two–scale Hamiltonian (1) with properly adjusted parameters \( a \) and \( b \) describes qualitatively and even quantitatively many physical effects. For example, it reproduces the oscillatory behavior in the free energy of interactions of two solute molecules as the function of their mutual distance, and gives with good precision the experimentally measured values of solvation free energy of alkane molecules [4].

However the Hamiltonian (1) is written \( \textit{ad hoc} \) on the basis of physical suppositions on the possibility of separation of interactions in “short” and “long” scales. If the two–length scale theory pretends to describe all the peculiarities of the hydrophobic effect, it should be confirmed by more solid arguments. For example, one could ask a question whether such a theory can be approved microscopically. Just this question is addressed in our paper. The results of our attempts to derive the Hamiltonian (1) from microscopic consideration are presented in Section III.

II. FROM MICROSCOPIC HAMILTONIAN TO DENSITY FUNCTIONAL

To make a contents of the paper as self–contained as possible, we describe in this section basic steps of passing from microscopic description of classical system with binary interactions to the pre-averaged description in terms of collective variables. The hydrophobic effect will be considered in Section III.

A. Collective variables

We begin with a partition function of a grand canonical ensemble for the system of \( n \) identical classical particles

\[
Z = \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \int \left( \prod_{i=1}^{n} d\mathbf{r}_i \right) e^{-\beta H_n} \tag{4}
\]

The Hamiltonian \( H_n \) of binary interacting particles has a standard form:

\[
H_n = \sum_{i=1}^{n} U(\mathbf{r}_i) + \sum_{i<j}^{n} V(\mathbf{r}_i - \mathbf{r}_j) \tag{5}
\]

where \( U(\mathbf{r}) \) is an external field and \( V(\mathbf{r} - \mathbf{r}') \) is a pairwise potential. The activity \( \lambda \) is related to the chemical potential \( \mu \) by the relation

\[
\lambda = \xi e^{\beta \mu}, \quad \xi = \frac{2\pi m kT}{\hbar^2}
\]

and \( \beta = 1/(kT) \) is the inverse temperature.

Let us define the density

\[
\rho(\mathbf{r}) = \sum_{i=1}^{n} \delta(\mathbf{r} - \mathbf{r}_i)
\]
Now we can pass from coordinates of individual particles, \( r_i \) \((i = 1, \ldots, n)\), to the pre-averaged local collective variables, \( \rho(r) \), via the standard technique of constraints in the functional integral. Using the relation
\[
\int \mathcal{D}\{\rho\} \delta\left[\rho(r) - \sum_{i=1}^{n} \delta(r - r_i)\right] = 1
\]
and the functional Fourier transform
\[
\delta\left[\rho(r) - \sum_{i=1}^{n} \delta(r - r_i)\right] = \int \mathcal{D}\{\phi\} \exp\left\{ i \int \phi(r) \left(\rho(r) - \sum_{i=1}^{n} \delta(r - r_i)\right) dr \right\}
\]
we get
\[
Z = \sum_{n=0}^{\infty} \int \mathcal{D}\{\phi\} \frac{\lambda^n}{n!} \int \prod_{i=1}^{n} dr_i \exp\left\{-i\beta \sum_{i=1}^{n} \phi(r_i)\right\} \times \int \mathcal{D}\{\rho(r)\} \exp\left\{i\beta \int dr \rho(r)\phi(r) - \beta \int dr \rho(r)U(r) - \frac{\beta}{2} \int dr dr' \rho(r)V(r - r')\rho(r')\right\}
\]
Carrying out the summation over \( n \) we obtain
\[
Z = \int \int \mathcal{D}\{\rho\} \mathcal{D}\{\phi\} e^{-S(\rho, \phi)}
\]
where
\[
S(\rho, \phi) = \frac{\beta}{2} \int \rho(r)V(r - r')\rho(r')drr' - \beta \int \rho(r)\left(\phi(r) - U(r)\right) dr - \lambda \int e^{-\beta \phi(r)} dr
\]
and \( \phi \) rotated to the imaginary axis. After the functional integration over the field \( \rho(r) \), we have
\[
Z = N \int \mathcal{D}\{\phi\} e^{-\tilde{S}(\phi)}
\]
where
\[
\tilde{S}(\phi) = -\frac{\beta}{2} \int \left(\phi(r) - U(r)\right)V^{-1}(r - r')\left(\phi(r') - U(r')\right) drr' - \lambda \int e^{-\beta \phi(r)} dr
\]
The equilibrium value of the field \( \phi \) can be directly obtained by minimizing the effective action, \( \tilde{S} \), of the system
\[
\frac{\delta \tilde{S}(\phi)}{\delta \phi} \bigg|_{\phi = \bar{\phi}} = \beta \lambda e^{-\beta \bar{\phi}(r)} - \beta \int V^{-1}(r - r') \left(\bar{\phi}(r') - U(r')\right) dr' = 0
\]
The mean density \( \bar{\rho}(r) \) is determined now by
\[
\bar{\rho}(r) = -\frac{1}{\beta} \frac{\delta \ln Z}{\delta U(r)}
\]
that reads
\[
\bar{\rho}(r) = \int V^{-1}(r - r') \left(\bar{\phi}(r') - U(r')\right) dr'
\]
After a little algebra we arrive at the nonlinear self-consistent equation for the average density \( \bar{\rho} \)
\[
\bar{\rho}(r) = \lambda \exp\left\{-\beta \left(U(r) + \int V(r - r')\bar{\rho}(r')drr'\right)\right\}
\]
The parameter \( \lambda \) and hence, \( \mu \), is determined by the value of \( \bar{\rho} \) in the bulk, \( \rho_b \). Rewritten in the terms of bulk density, \( \bar{\rho} \) reads
\[
\bar{\rho}(r) = \rho_b \exp\left\{-\beta \left(U(r) + \int V(r - r')\left(\bar{\rho}(r') - \rho_b\right) drr'\right)\right\}
\]
B. Free energy functional

Equations (12), (14) and (15) are sufficient to obtain an explicit expression of \( \bar{\rho} \) and of thermodynamic functionals \( \Omega \) and \( F \). In the saddle point approximation the grand thermodynamic potential \( \Omega \) is

\[
\Omega = -\frac{1}{\beta} \ln Z = S\{\bar{\phi}\} \tag{17}
\]

Using (14) and (15), we obtain

\[
\Omega = -\frac{1}{2} \int \bar{\rho}(r)V(r-r')\bar{\rho}(r')dr' - \frac{1}{\beta} \int \bar{\rho}(r)dr \tag{18}
\]

From (15) we can easily get the chemical potential

\[
\mu = \frac{1}{\beta} \ln \bar{\rho}(r) + U(r) + \int V(r-r')\bar{\rho}(r')dr' + \text{const} \tag{19}
\]

(we can remove the constants in (19), because they determine only the reference state and do not give any contribution to physically important quantities). Recalling that

\[
F = \Omega + \int \mu(\rho)\rho(r)dr \tag{20}
\]

we arrive at the following expression for the free energy functional, \( F \)

\[
F = \frac{1}{2} \int \bar{\rho}(r)V(r-r')\bar{\rho}(r')dr' + \frac{1}{\beta} \int \bar{\rho}(r)(\ln \bar{\rho}(r) - 1)dr + \int U(r)\bar{\rho}(r)dr \tag{21}
\]

The grand canonical potential \( \Omega \) determined by (18) depends on density distribution \( \bar{\rho}(r) \) only, while from the "thermodynamic viewpoint" it should be the function of \( \mu \). Taking into account that according to (19) the chemical potential \( \mu \) in (18) is expressed already as a function of \( \bar{\rho} \), we can reconstruct the thermodynamically consistent form of \( \Omega \). Starting from the free energy functional (21) and applying Legendre transform, we obtain the grand canonical potential with explicit dependence on \( \mu \):

\[
\Omega = \frac{1}{2} \int \bar{\rho}(r)V(r-r')\bar{\rho}(r')dr' + \frac{1}{\beta} \int \bar{\rho}(r)(\ln \bar{\rho}(r) - 1)dr + \int U(r)\bar{\rho}(r)dr - \mu \int \bar{\rho}(r)dr \tag{22}
\]

C. Correlation and response functions

There are several equivalent ways that allow to obtain the correlation function from density functional [6]. We use the procedure based on variation of the density of a liquid with respect to an external potential \( U(r) \). According to [6] the one-point (direct) correlation function \( c^{(1)}(r) \) can be defined via the following relation

\[
\rho(r) = \lambda \exp\left\{ -\beta U(r) + c^{(1)}(r) \right\} \tag{23}
\]

Comparing (23) and (15), we arrive at the following explicit expression for \( c^{(1)}(r) \):

\[
c^{(1)}(r) = -\beta \int V(r-r')\bar{\rho}(r')dr' \tag{24}
\]

Exploiting standard relation (see, for example, [6])

\[
c^{(2)}(r,r') = \frac{\delta c^{(1)}(r)}{\delta \rho(r')} \tag{25}
\]

we get

\[
c^{(2)}(r,r') = -\beta V(r-r') \tag{26}
\]
here $c^{(2)}(r)$ is the well-known Orstein–Zernike direct correlation function. The inverse response function $\chi(r, r')^{-1}$ reads

$$\chi(r, r')^{-1} = \frac{\delta(r - r')}{\rho(r)} - c^{(2)}(r, r') = \frac{\delta(r - r')}{\rho(r)} + \beta V(r - r') \quad (27)$$

The connection to experimentally accessible quantities is established by means of the following equations

$$\chi(|r - r'|) = \rho_0 \delta(r - r') + \rho_0^2 h(|r - r'|); \quad \int \chi(|r - r''|)\chi^{-1}(r'', r') d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r'}) \quad (28)$$

where $h(r) = g(r) - 1$ is the experimentally measurable correlation function of the pure liquid.

Let us mention that the results (27)–(28) can be obtained by exploiting an exact relation known as the first Yvon equation [3] and (28), i.e.

$$h(r, r') = \frac{-kT}{\rho(r)\rho(r')} \frac{\delta \rho(r)}{\delta U(r')} - \frac{\delta(r - r')}{\rho(r')}$$

In case of more sophisticated form of entropy term (see III C) some modifications have to be introduced in (27). Namely

$$\chi(r, r')^{-1} = \frac{\rho_0 \delta(r - r')}{\rho(r)(\rho_0 - \rho(r))} + \beta V(r - r') \quad (29)$$

while the equation (28) remains without any changes.

### III. FROM MICROSCOPIC APPROACH TO GINZBURG–LANDAU–CHANDLER–TYPE THEORY

In principle, the partition function (1) describes all physical properties of a liquid, including the possible phase transitions, while the mean–field free energy functional (21) has a single minimum and hence does not describe phase transition. This contradiction is due to the point–like nature of particles in our treatment. We can overcome this obstacle introducing a finite size for each particle. This is done in the Section III C. In the meantime, in Sections IIIA IIIB we split the free energy functional (21) in long– and short–ranged parts and derive the solvation free energy using the technique of constraints in the functional integral.

#### A. Expansion of the free energy

Consider a solution $\bar{\rho}(r) \equiv n(r)$ describing an equilibrium liquid–vapor interface. Supposing that the continuous profile $n(r)$ is rippled by fluctuations [3], write the instantaneous value of the density as a sum of two parts: $\rho(r) = \omega(r) + n(r)$, where $n$ corresponds to an equilibrium interface and $\omega$ – to fluctuations. Expand now the grand thermodynamic potential near the profile $n(r)$ in $\omega(r)$ up to the second order. This is possible if the fluctuations only slightly deform the equilibrium profile. Thus, we have

$$\Omega[\rho] = \Omega[n] + \int \frac{\delta \Omega}{\delta \rho(r)} \bigg|_{\rho=n} \omega(r) \, d\mathbf{r} \quad + \quad \frac{1}{2} \int \frac{\delta^2 \Omega}{\delta \rho(r)\delta \rho(r')} \bigg|_{\rho=n} \omega(r)\omega(r') \, d\mathbf{r} d\mathbf{r}' \quad (30)$$

By definition:

$$\frac{\delta \Omega}{\delta \rho(r)} \bigg|_{\rho=n} = 0, \quad \frac{\delta^2 \Omega}{\delta \rho(r)\delta \rho(r')} \bigg|_{\rho=n} = \chi^{-1}(r - r') \quad (31)$$

Substituting (31) into (30), we get

$$\Omega[\rho] = \Omega[n] + \frac{1}{2} \int \omega(r)\chi^{-1}(r - r')\omega(r') d\mathbf{r} d\mathbf{r}' \quad (32)$$
The density distribution $n(r)$ is long–ranged, so its Fourier image $n(k)$ is nonzero at small $k$. Using this fact we can simplify (32) in the following manner. Consider the part of the Fourier space where $n(k) \neq 0$. In this region $V(k)$ can be expanded in a Taylor series: $V(k) \simeq v_0 + k_i \partial_i V(k) + \frac{1}{2} k_i k_j \partial_i \partial_j V(k)$ ($\{i, j\} = 1, 2, 3$). Under the symmetry arguments the last expression reduces to

$$V(k) \simeq v_0 + \frac{1}{2} \nu_2 k^2$$

So, we get

$$\int n(r)V(r-r')n(r')dr'dr = v_0 \int n^2(r)dr + \frac{\nu_2}{2} \int (\nabla n(r))^2 dr$$

where

$$v_0 = \int V(r)dr, \quad \nu_2 = -\int r^2 V(r)dr \tag{33}$$

Thus, $\Omega[n]$ appears as:

$$\Omega[n] = \frac{1}{\beta} \int n(r)(\ln n(r) - 1)dr + \frac{v_0}{2} \int n^2(r)dr + \frac{\nu_2}{4} \int (\nabla n(r))^2 dr \tag{34}$$

Collecting all terms we obtain a mean–field Ginzburg–Landau–Chandler–type functional

$$\Omega = \frac{1}{2} \int \omega(r)\chi^{-1}(r-r')\omega(r')drdr' + \int \left\{ \frac{\nu_2}{4} (\nabla n(r))^2 + \tilde{W}(n(r)) \right\} dr \tag{35}$$

where

$$\tilde{W}(n(r)) = \frac{v_0}{2} n^2(r) + \frac{1}{\beta} n(r)(\ln n(r) - 1) - \mu n(r) \tag{36}$$

One can clearly see the similarity between (35)–(36) and (1)–(2). As it has been mentioned in the Introduction, the precise form of the potential $\tilde{W}(n(r))$ is not important – it should only allow the phase transition. Despite $\tilde{W}(n(r))$ does not fit this condition, its simple generalization obtained in Section II C in the frameworks of the same formalism satisfies all necessary requirements. The interaction term between fluctuations of short– and long–ranged fields identically vanishes in (35), so the coupling constant $c$ in (1) should be assigned to zero.

The difference between the microscopic approach considered in this paper and the approach based on scale separation becomes much more essential when we put the solute molecule into the solvent described by the Hamiltonian (5) and apply the technique of functional constraints as it has been proposed by Li and Kardar and then exploited by Chandler et al.

### B. The cavitation part of the solvation free energy

The influence of cavities, extended surfaces and other inhomogeneities of geometric origin immersed in fluctuating environment, can be taken into account by means of a technique of constraints in functional integration. In brief, the presence of a constraint in a partition function generates an artificial "ghost" field coupled with other "real" fields describing the fluctuating media. This interaction corresponds to the media (solvent) response on a constraint. In particular, the cavitation part of a hydrophobic effect appears due to the requirement to have no solvent particle inside the fixed cavity (solute molecule).

In this Section we start with the microscopic Hamiltonian (5) and pass to the collective variables (as it has been done in section II) demanding that no particle enter the volume $V_{in}$ of a solute molecule. The corresponding partition function can be written as follows

$$Z = \int \mathcal{D}\{\rho\} \mathcal{D}\{\phi\} \prod_{r \in V_{in}} \delta[\rho] e^{-S(\rho, \phi)} \tag{37}$$
where the action $S$ has the form

$$
S\{\rho, \phi\} = \frac{\beta}{2} \int \rho(r)V(r - r')\rho(r')drdr' - \beta \int \rho(r)(\phi(r) - U(r))dr - \lambda \int e^{-\beta\phi(r)}dr
$$

(38)

Using again the functional Fourier representation of $\delta$–function and rotation of $\psi$ to the imaginary axis, we get

$$
Z = N_1 \int \mathcal{D}\{\phi\}\mathcal{D}\{\psi\} \exp \left\{ \frac{\beta}{2} \int drdr' \left( \phi(r) - U(r) \right) V^{-1}(r - r')(\phi(r') - U(r')) \right\} + \lambda \int d\epsilon e^{-\beta\phi(r)} \right\}
$$

(39)

Integrating over the fields $\rho$ and $\psi$, we arrive at the following expression

$$
Z = N_2 \int \mathcal{D}\{\phi\} \exp \left\{ \frac{\beta}{2} \int drdr' \left( \phi(r) - U(r) \right) V^{-1}(r - r')(\phi(r') - U(r')) + \lambda \int d\epsilon e^{-\beta\phi(r)} \right\}
$$

(40)

where

$$
\int_{v_{in}} dr'' V_{in}(r, r'') V(r'' - r') = \delta(r' - r) \quad \text{for } r, r' \in v_{in},
$$

$$
V_{in}(r, r'') = 0 \quad \text{for } r \in v_{out}.
$$

Introducing the new variable

$$
\bar{\vartheta}(r) = \int V(r - r')(\phi(r') - U(r'))dr'
$$

(41)

the partition function can be rewritten as

$$
Z = N_3 \int \mathcal{D}\vartheta e^{-\tilde{S}\{\vartheta\}}
$$

(42)

where

$$
\tilde{S}\{\vartheta\} = \frac{\beta}{2} \int \bar{\vartheta}(r)V(r - r')\bar{\vartheta}(r')drdr' - \frac{\beta}{2} \int \bar{\vartheta}(r)V_{in}(r, r')\bar{\vartheta}(r')drdr' + \lambda \int \exp \left\{ -\beta \left( U(r) + \int V(r - r')\bar{\vartheta}(r')dr' \right) \right\}
$$

(43)

In a saddle point approximation we have

$$
\frac{\delta \tilde{S}\{\vartheta\}}{\delta \vartheta} = \beta \int V(r - r')\bar{\vartheta}(r')dr' - \beta \int V_{in}(r, r')\bar{\vartheta}(r')dr' - \beta \lambda \int V(r - r') \exp \left\{ -\beta \left( U(r') + \int V(r' - r'')\bar{\vartheta}(r'')dr'' \right) \right\} dr' = 0
$$

(44)

Calculating now the mean density $\bar{\rho}(r)$ in a standard manner, we arrive at the following expression

$$
\bar{\rho}(r) = \lambda \exp \left\{ -\beta \left( U(r) + \int V(r - r')\bar{\vartheta}(r')dr' \right) \right\}
$$

(45)

where $\bar{\vartheta}(r)$ is defined from

$$
\bar{\rho}(r) - \int V^{-1}(r - r')V_{in}(r', r'')\bar{\vartheta}(r'')dr'' = \lambda \exp \left\{ -\beta \left( U(r) + \int V(r - r')\bar{\vartheta}(r')dr' \right) \right\}
$$

(46)
Let us pay attention to the equations (45)–(46) obtained using the standard technique of functional constraints with the microscopic Hamiltonian before separation of the density field $\rho(r)$ into short- and long-ranged scales. The equation (46) is contradictory to some extent. Namely, for all $r \in v_\text{in}$ the left-hand side of (46) identically vanishes, while the right-hand side is positive. This contradiction can be formally removed by noting that the potential $U$ creates an impenetrable wall around the volume $v_\text{in}$. However, in this case the value of the field $\bar{v}$ is undetermined inside the volume $v_\text{in}$.

So, the account of hydrophobic effect by natural inserting constraint into the functional integral leads to internal inconsistency in the two–length scale theory. One can overcome this contradiction by using the two–length scale expansion on the first step, and applying the functional constraint on the subsequent step, against the direct use of constraint on microscopic level as in (37), however such a procedure looks a bit artificial.

C. Solvent particles of finite volume

The simplest way to take into account the finiteness of the volume occupied by particles of the solvent consists in introducing an additional artificial density $\rho_\text{v}(r)$ associated with voids between particles, and requiring then the sum of two densities, $\bar{\rho}(r)$ and $\rho_\text{v}(r)$ to be constant everywhere. Such a condition guarantees that when a particle leaves some volume, it is replaced by a "hole". Such consideration is a sort of an off–lattice Flory–Huggins mean-field treatment. Following the same steps as in the Section 11 we arrive finally at the free energy functional, which generates the grand potential functional with a double–well structure, describing a phase transition:

$$F = \frac{1}{2} \int \rho(r)V(r-r')\bar{\rho}(r')dr' + \frac{1}{\beta} \int \bar{\rho}(r)\ln\bar{\rho}(r)dr + \frac{1}{\beta} \int \left(\rho_\text{v}(r) - \bar{\rho}(r)\right)\ln\left(\rho_\text{v}(r) - \bar{\rho}(r)\right)dr + \int U(r)\bar{\rho}(r)dr$$

(47)

where $\rho_\text{v}(r) = \rho_0 - \bar{\rho}(r)$ and $\rho_0$ is the inverse volume of a media molecule. Rewriting the entropy term, neglecting the meaningless constants and proceeding to the grand potential $\Omega$, we get:

$$\Omega = \frac{\rho_0}{\beta} \int \frac{\bar{\rho}(r)}{\rho_0} \ln\frac{\bar{\rho}(r)}{\rho_0} + \left(1 - \frac{\bar{\rho}(r)}{\rho_0}\right)\ln\left(1 - \frac{\bar{\rho}(r)}{\rho_0}\right)dr + \frac{1}{2} \int \bar{\rho}(r)V(r-r')\bar{\rho}(r')dr' - \int \mu\bar{\rho}(r)dr + \int U(r)\bar{\rho}(r)dr$$

(48)

The equilibrium density profile is determined by the condition

$$\frac{\delta\Omega}{\delta\rho(r)} = 0$$

(49)

which leads to the following equation:

$$\bar{\rho}(r) = \left(\rho_0 - \bar{\rho}(r)\right)\exp\left(\beta \left(\mu - U(r) - \int V(r-r')\bar{\rho}(r')dr'\right)\right)$$

(50)

Let us focus attention on the structure of $\Omega$. There are two independent parameters, namely $\beta$ and $\mu$, which determine the thermodynamic state of the system. In a homogeneous media the density of the grand thermodynamic potential may be written as

$$-p = \frac{\rho}{\beta} \ln\frac{\rho}{\rho_0} + \rho_0 \left(1 - \frac{\rho}{\rho_0}\right) + \frac{1}{2} \nu_0 \bar{\rho}^2 - \mu\bar{\rho}$$

(51)

The quantity $\nu_0$ is determined by (33). It is easy to see that (51) describes the phase coexistence when $\mu_c = \rho_0\nu_0/2$. Then the critical temperature $T_c$ of the vapor–liquid phase transition is determined by $\partial^2p/\partial\rho^2 = 0$, giving $T_c = -\nu_0\rho_0/4$. Below $T_c$ there are two different phases, while above $T_c$ the system is homogenous. Other values of $\mu$ correspond to cases of single phase in the system, vapor or liquid. The value of $\rho_0$ is fixed by the bulk density $\rho_b$. Sufficiently far from the solvated object $U(r) \simeq 0$, thus we have:

$$\ln\left(\frac{\rho_0}{\rho_0 - \rho_b}\right) = \nu_0 \left(\frac{\rho_0 - \rho_b}{2}\right)$$

(52)

As was mentioned above the parameter $\rho_0$ is related to the inverse volume of the molecule. The latter is rather arbitrary, because it strongly depends on the convention how the intra–molecular potential is divided into repulsive and attractive parts. Let us stress that in our approach we do not use explicitly the pairwise potential of liquid molecules $V(r-r')$, it enters effectively only through the correlation function $h(r-r')$—see (27)–(28). For example, we can associate the parameter $\rho_0$ with the repulsive part of potential and the $V(r-r')$ – with the smooth attractive part. So, one can say that the relation (52) fixes the value of $\rho_0$, while the correlation function of the liquid $h(r-r')$ fixes the potential $V(r-r')$ via (28).
IV. DISCUSSION

The aim of the present paper is two-fold. On one hand, we have derived the self-consistent set of equations which determine the solvation free energy of a molecule of arbitrary shape immersed into a solution. The shape of a solute molecule is completely defined by the collection of its Van-der-Waals radii and is encoded in the potential $U(r)$ coupled to the equilibrium solvent density $\bar{\rho}(r)$. In turn, the equilibrium density $\bar{\rho}(r)$ is determined by the nonlinear equation containing the pairwise density–density correlation function, $\chi(r - r')$ of a pure solvent, which is supposed to be known and serves as an input in the theory. The full set of corresponding equations is collected below for convenience:

$$
\begin{align*}
F &= \frac{1}{2} \int \bar{\rho}(r)V(r - r')\bar{\rho}(r')dr'dr + \frac{1}{\beta} \int \bar{\rho}(r)\ln(\bar{\rho}(r))dr + \frac{1}{\beta} \int (\rho_0 - \bar{\rho}(r))\ln(\rho_0 - \bar{\rho}(r))dr + \int U(r)\bar{\rho}(r)dr \\
\bar{\rho}(r) &= (\rho_0 - \bar{\rho}(r))\exp\left\{\frac{\beta}{2} \left[ \int V(r)dr - U(r) - \int V(r - r')\bar{\rho}(r')dr' \right] \right\} \\
V(r - r') &= \frac{1}{\beta} \chi(r, r')^{-1} - \frac{\rho_0 \delta(r - r')}{\beta \rho(r)(\rho_0 - \rho(r))}
\end{align*}
$$

(53)

The correlation function $\chi(r - r')$ and the density $\rho_0$ in the bulk enter as inputs in the theory, while the relation between the constants $\rho_0$ and $\rho_b$ is established in (52). Let us stress that the free energy of interactions between different solute molecules can be straightforwardly computed on the basis of (53).

On the other hand, we have established the internal inconsistency between the microscopic approach and the two–ranged scale Ginzburg–Landau–Chandler (GLC) description of hydrophobic effect.

Let us remind that the Hamiltonian of the GLC–type theory consists of two phenomenological parts: (i) the nonlocal Gaussian term corresponding to short–ranged interactions between pure solvent molecules in the bulk, and (ii) the ”long–ranged” term coming from smoothly changing profile of ”macroscopic” (i.e. averaged over short–ranged fluctuations) solvent density taken in a form of a Ginzburg–Landau expansion. These two contributions to the free energy are decoupled until the solute molecule is put into a solvent. In the frameworks of GLC theory the solute expels the total solvent density $\rho(r)$ from the volume. As soon as $\rho(r)$ is a sum of short– and long–ranged contributions, the condition $\rho(r) = 0$ inside the solvent molecule leads to an effective coupling between short– and long–ranged fields. Then one can proceed with the standard thermodynamic formalism and compute the averaged density, the solvation free energy, etc.

The origin of the discrepancy between microscopic approach developed above and GLC–type theory consists in the following. If we use the functional constraint nullifying the total solvent density $\rho$ (as in GLC theory) in the partition function with microscopic Hamiltonian (see eq. (52)), then we come to the contradiction: some fields entering in the answer cannot be accurately defined (for more details see the last paragraph of Section III B). Only for pure solvent the decomposition on short– and long–ranged scales (as in GLC approach) is consistent with microscopic description—compare (35–36) and (11–2). At the same time the approach described in the current paper does not require any coupling between fields describing the microscopic and macroscopic structures of the solvent—in our work we get rid of any artificial division of fields in different scale ranges. Moreover, the values of the coefficients $a$ and $b$ in the GLC Hamiltonian are not arbitrary, but are dictated by theory (35).

Meanwhile, we consider it necessary to note that still the two–length scale model, being properly tuned, provides rather successful quantitative description of cavitation part of hard spheres and the solvation energies of alkane molecules as it has been shown recently, for example, in [1]. So, to our point of view the GLC–type approach is nevertheless satisfactory as a phenomenological theory.

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