

Research Article

J-Potential in Classical Thermodynamics and Its Application to a Critical Vapor Bubble in a Metastable Liquid

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Abstract: The article introduces the reader to the thermodynamic potential of classical thermodynamics, called the *J*-potential. It can be generally defined as the grand thermodynamic potential plus the volume of the system multiplied by some pressure (which may be the external pressure, the pressure in one of the phases in a multiphase system). Variants of the *J*-potential are considered. It is shown that the *J*-potential is perfectly suited for multiphase (heterogeneous) systems. In this work, it is applied to study the dependence of the chemical potential of a substance in a small vapor bubble, formed in the bulk liquid, on the bubble size.

Keywords: thermodynamic potential, characteristic function, fundamental equations, hybrid thermodynamic potential, *J*-potential, bubble

Nomenclature

Latin letters

A	Area (of the interfacial surface)
a	A mean-field attraction parameter in the fluid, used in the gradient Density Functional Theory (DFT)
C	A squared-gradient coefficient in the gradient DFT
F, f	Free energy, its bulk density F/V
G	The Gibbs energy (Gibbs potential)
H	Enthalpy
i, j	Subscript indices, numerating the components in a multicomponent system
J, J_c	<i>J</i> -potential, classical <i>J</i> -potential
k, s, t	Superscript indices, numerating the phases, interfacial surfaces and contact lines;
k_B	The Boltzmann constant
L	Length (of the interfacial contact line)
N	Number of molecules
\mathbf{P}	Vector of the local external force (stress)

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p	Pressure
R, R'	Radius of the bubble (for the surface of tension, for the equimolecular surface)
\mathbf{r}, r	Radius-vector, distance from the origin (the center of the bubble)
S, s	Entropy, its bulk density S/V
T	Temperature
U	Internal energy
\mathbf{u}	Local displacement vector of the system surface
V	Volume
W	Work
w	Long-range intermolecular attraction potential

Greek letters

α, β	Phases (α — bubble/droplet, β — bulk medium), used in superscripts to mark the bulk quantities
Γ	Adsorption, the surface excess of number of molecules per unit area
γ	Surface tension
$\Delta\mu$	The chemical potential shift from its value at the binodal, $\mu - \mu_\infty$
δ	The Tolman length; a small change; a variation (of a function or a functional)
μ	Chemical potential
ρ	Bulk number density of molecules N/V
τ	Line tension
χ	Isothermal compressibility
Ω	Grand potential

Common modifiers

\sim	Mark the hybrid potentials (with the μ - N Legendre transformation made with respect to some, but not all, variables)
$\overline{}, \overline{\overline{}}$	Overline marks the surface excess, double overline — the line excess of the quantity

Common subscripts

hs	Refers to the ideal system of hard spheres
∞	Refers to the value at the binodal (liquid–gas coexistence with a planar interface)

1. Introduction

Thermodynamics, the most important of the sciences of the 19th century, looks rather modest now, but its importance has by no means diminished, and it remains an important factor in the formulation of many modern sciences. The face of classical equilibrium thermodynamics has changed, thanks to the work of Gibbs,^{1,2} in two respects. First, pre-Gibbsian thermodynamics was the thermodynamics of cycles. This calculation method was ubiquitous, but completely disappeared (after the first third of the 20th century) after the spread of Gibbs' thermodynamic potentials. The calculation of the work of a process using thermodynamic potentials is straightforward: this work is equal to the change in the appropriate thermodynamic potential under conditions corresponding to the process. Secondly, after Gibbs introduced the concept of chemical potential (the main physical quantity of chemistry), his thermodynamics is often called chemical. Chemical thermodynamics takes into account the change in the state of a system after a change in the quantities of its components, both as a result of their addition and in the course of chemical reactions. With the introduction of the chemical potential, the transition from closed systems (for which thermodynamics was developed at the beginning) to open systems is associated. Although Gibbs did not apply the concept of chemical potential to a solid, he showed that if this were done, then the chemical potential of a solid must be a tensor quantity, since a solid can be in

equilibrium simultaneously with three of its different solutions in different directions. Here, for simplicity, we will limit our consideration to fluids and will write down all the formulas for open fluid systems.

The main quantities of thermodynamics are the characteristic functions, by differentiation of which all thermodynamic parameters can be obtained (which is fixed in the fundamental thermodynamic equations). All thermodynamic potentials are characteristic functions, but not vice versa. For example, entropy is a characteristic function, but not a thermodynamic potential. A harmonious system of Gibbsian thermodynamics is built starting from the energy U , more precisely from its fundamental equation

$$\delta U = T\delta S + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \delta W + \sum_i \mu_i \delta N_i \quad (1)$$

with S the entropy of the system, T the absolute temperature, A the area of the external surface of the system, \mathbf{P} the local vector of the external force (called stress) applied to the unit of this external surface, \mathbf{u} the local displacement vector of this surface. The scalar product $\mathbf{P} \cdot \delta \mathbf{u}$ gives the elementary work of displacement of a unit surface area. The integration is performed over the most closed surface (A) of the system. The last term includes chemical potentials μ_i and changes δN_i in the number of molecules of the system components, i numbers the system components. Together, the second and third terms on the right hand side of Equation (1) are the work done by external forces on the system. From it, in the form of the second term, mechanical work is singled out separately, so that δW reflects all other types of work. If the system is surrounded by a homogeneous external environment (e.g., the atmosphere) with pressure p (pressure and stress are always opposite in sign), then the second term is reduced to the well-known expression $-pdV$ with V the volume of the system.

Thus, the whole Equation (1) expresses the meaning of the first law of thermodynamics: an increase in the energy of a closed system is achieved by the influx of heat (written here, as is customary in equilibrium thermodynamics, in the form $T\delta S$) and the performance of work on the system with external bodies. Equation (1) implies the condition

$$\delta U = \delta W \quad (\delta S = 0, \delta \mathbf{u} = 0, \delta N_i = 0), \quad (2)$$

indicating that the internal energy is a thermodynamic potential at fixed entropy, boundaries of the system and quantities of all components.

Let us briefly recall other thermodynamic potentials. The free energy (adding the word ‘‘Helmholtz’’ is no longer accepted) F is defined as

$$F \equiv U - TS. \quad (3)$$

From Equations (1) and (3), we immediately obtain

$$\delta F = -S\delta T + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \delta W + \sum_i \mu_i \delta N_i, \quad (4)$$

and it follows from Equation (4)

$$\delta F = \delta W \quad (\delta T = 0, \delta \mathbf{u} = 0, \delta N_i = 0), \quad (5)$$

that the free energy is a thermodynamic potential at constant temperature, quantities of all components and fixed boundaries of the system. Since isothermal processes are more often dealt with than adiabatic ones, the free energy is a more practical thermodynamic potential than the energy.

The next thermodynamic potential, the Gibbs energy G (Gibbs free energy, Gibbs thermodynamic potential), is well known for the case of a system surrounded by a homogeneous medium with a given pressure p :

$$G \equiv F + pV \equiv U - TS + pV. \quad (6)$$

However, the definition of G is ambiguous in the general case. Based on Equation (1), we can use the definition

$$G \equiv U - TS - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA. \quad (7)$$

From Equations (1) and (7), we find

$$\delta G \equiv -S\delta T - \oint_{(A)} (\delta \mathbf{P} \cdot \mathbf{u}) dA + \delta W + \sum_i \mu_i \delta N_i. \quad (8)$$

From here, the condition follows

$$\delta G = \delta W \quad (\delta T = 0, \delta \mathbf{P} = 0, \delta N_i = 0), \quad (9)$$

which means that the Gibbs energy is a thermodynamic potential at constant temperature, external stresses and quantities of all components. If atmospheric pressure is the only external stress, then, under conditions of a laboratory experiment, the Gibbs energy in the form of (6) is the only one suitable for calculating the work. This seems to be the most popular thermodynamic potential.

Let us move on to the enthalpy H . This quantity is widely known as a heat function and, it would seem, has nothing to do with work. However, there are conditions when enthalpy can also play the role of a thermodynamic potential. Let us find these conditions. The definition of enthalpy is known only for a system in a medium with a constant pressure p :

$$H \equiv U + pV. \quad (10)$$

Similarly to Equation (7), the enthalpy of a body of any nature and with an arbitrary distribution of external forces on it can be defined as

$$H \equiv U - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA. \quad (11)$$

By varying Equation (11) and substituting Equation (1) into it, we find

$$\delta H \equiv T\delta S - \oint_{(A)} (\delta \mathbf{P} \cdot \mathbf{u}) dA + \delta W + \sum_i \mu_i \delta N_i, \quad (12)$$

from which it follows

$$\delta H = \delta W \quad (\delta S = 0, \delta \mathbf{P} = 0, \delta N_i = 0). \quad (13)$$

The condition expressed in Equation (13) confirms that enthalpy can indeed be a thermodynamic potential at fixed entropy, quantities of all components and all external forces.

It is of note that the described thermodynamic potentials U , F , G and H are all such only for closed systems. In Gibbs' work "On the Equilibrium of Heterogeneous Substances" (1876),^{1,2} they were described as characteristic functions and were not used to calculate the work. Subsequently, Gibbs took up statistical mechanics for closed and open systems, and hence for open systems comes the fifth thermodynamic potential Ω , which we call the "grand thermodynamic potential" because it is associated with the grand canonical distribution. For it there is a strict definition

$$\Omega \equiv U - TS - \sum_i \mu_i N_i \equiv F - \sum_i \mu_i N_i. \quad (14)$$

Varying Equation (14) and substituting Equation (1), we find the fundamental equation for Ω

$$\delta\Omega = -S\delta T + \oint_{(A)} (\mathbf{P} \cdot \delta\mathbf{u}) dA + \delta W - \sum_i N_i \delta\mu_i. \quad (15)$$

From here, it follows

$$\delta\Omega = \delta W \quad (\delta T = 0, \delta\mathbf{u} = 0, \delta\mu_i = 0). \quad (16)$$

Equation (16) indicates that Ω works as a thermodynamic potential at constant temperature, boundaries of the system and chemical potentials.

As is known, for a homogeneous (single-phase) system, the five considered thermodynamic potentials in the absence of other (non-mechanical) types of work ($\delta W = 0$) are written as

$$U = TS - pV + \sum_i \mu_i N_i, \quad (17)$$

$$F = -pV + \sum_i \mu_i N_i, \quad (18)$$

$$G = \sum_i \mu_i N_i, \quad (19)$$

$$H = TS + \sum_i \mu_i N_i, \quad (20)$$

$$\Omega = -pV. \quad (21)$$

It can be seen from this list of formulas that each thermodynamic potential is obtained by subtracting some terms from Equation (17), which corresponds to the Legendre transformation(s). But, when we get to Equation (21), there is nothing more to subtract. Thus, Equations (17)–(21) are a complete list of the main thermodynamic potentials for a homogeneous system.

A further increase in the number of thermodynamic potentials for a homogeneous system can only be associated with the modification of Equations (17)–(21). So, when passing from Equation (18) to Equation (21), we subtract the entire sum, but it is possible to subtract only some of its terms. If we arbitrarily divide the components of the system into two groups with indices k and j and subtract from Equation (18) only the sum of the group k , then we get

$$\tilde{\Omega} = -pV + \sum_j \mu_j N_j, \quad \sum_i \mu_i N_i = \sum_k \mu_k N_k + \sum_j \mu_j N_j, \quad (22)$$

where the new thermodynamic potential $\tilde{\Omega}$ plays the role of free energy with respect to the components of group j and the role of grand thermodynamic potential with respect to the components of group k (such thermodynamic potentials are called hybrid³⁻⁷ or mixed^{8,9}). The hybrid thermodynamic potential is of great practical importance for systems with solids, when the j group refers to the immobile components of the solid, and the k group refers to the mobile components of the surrounding solution, as demonstrated in previous applications.⁷⁻⁹ In particular, it is important for mechanochemistry.^{10,11}

The foregoing referred to homogeneous (single-phase) systems. For heterogeneous systems, where, in addition to phases, there are also interfacial surfaces, the situation is different. The expression for the grand thermodynamic potential (21) in this case takes the form

$$\Omega = \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA, \quad (23)$$

and from here it is quite possible to subtract $-pV$. In this way, a new thermodynamic potential was introduced, called the J -potential.^{12,13} In fact, the J -potential is a whole class of new thermodynamic potentials for heterogeneous systems. The purpose of this article is to introduce the reader to the J -potential and, as an example, demonstrate its application to solve a specific physical problem. As such, we chose the study of the dependence of the chemical potential of a substance in a gas bubble on the size of the bubble. Definition and discussion of the J -potential for systems containing solids can be found in other articles.^{13,14}

2. J -potentials

As we agreed above, in this article, for simplicity, we restrict ourselves to consideration of fluid systems. For them, the approach to introducing J -potentials was recently developed,¹⁵ and we will follow this approach. The most general definition of the J -potential can be formulated in terms of the grand thermodynamic potential Ω as follows:

$$J \equiv \Omega + p'V, \quad (24)$$

with V the volume of the system, and p' some pressure chosen for reasons of convenience. For example, it can be an external pressure p (the classic case, then the J -potential is denoted as J_c) or the pressure in one of the phases of a heterogeneous system. The latter, in addition to phases, also has interfacial surfaces with surface tension γ and interfacial lines with line tension τ . For an arbitrary heterogeneous system, the grand thermodynamic potential can be decomposed into

$$\Omega = -\sum_k p^k V^k + \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \quad (25)$$

where k numbers the bulk phases with volumes V^k , s numbers the interfaces with areas A^s , and t numbers the lines with lengths L^t . Substituting Equation (25) into Equation (24) gives an expression for the J -potential of a heterogeneous system

$$J = -\sum_k (p^k - p') V^k + \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \quad (26)$$

where the obvious relation has been taken into account $V = \sum_k V^k$.

In a simple case of a single-phase bulk fluid, the grand thermodynamic potential is given by Equation (21) and, thus,

$$J = (p' - p)V. \quad (27)$$

The classical J -potential, J_c , corresponding to the choice $p' = p$ then simply equals zero in this homogeneous system. But this is not the case for an inhomogeneous and/or multiphase system, where the grand thermodynamic potential is given by a more general Equation (23) or/and can be decomposed into several bulk parts and also surface and (where applicable) line excesses as given by Equation (25). In such a case, even a classical J -potential, J_c , given by Equation (26) at $p' = p$, does not generally equal zero.

Let us also give a differential fundamental equation for the J -potential. To do this, we need to recall a similar equation for the grand thermodynamic potential¹⁵

$$d\Omega = -SdT - \sum_i N_i d\mu_i - pdV + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \quad (28)$$

Differentiating Equation (24) and substituting Equation (28) into it, we obtain

$$dJ = -SdT - \sum_i N_i d\mu_i + (p' - p)dV + Vdp' + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \quad (29)$$

In particular, for the classical J -potential ($p' = p$) we have

$$dJ_c = -SdT - \sum_i N_i d\mu_i + Vdp + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \quad (30)$$

In accordance with Equation (29), the equilibrium condition is written in terms of the J -potential as

$$(dJ)_{T, \mu_i, V, p', A^s, L^t} = 0. \quad (31)$$

It follows the general Gibbs equilibrium principle applicable to any thermodynamic potential (see a detailed discussion in section 23 in reference 16).¹⁶

Let us now introduce the hybrid J -potential (denoted as \tilde{J}). To do this, we divide the system components into two groups, j and k , and substitute the hybrid grand thermodynamic potential, according to Equation (22), into definition expressed in Equation (24):

$$\tilde{J} = \tilde{\Omega} + p'V = \sum_j \mu_j N_j - \sum_k (p^k - p')V^k + \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \quad (32)$$

$$d\tilde{J} = -SdT - \sum_i N_i d\mu_i + \sum_j \mu_j dN_j - (p - p')dV + Vdp' + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \quad (33)$$

Here one can also distinguish between the classical hybrid J -potential (for $p' = p$) and special hybrid J -potentials (for different choices of p'). Fundamental equations (32) and (33) for the classical hybrid J -potential are simplified to the form

$$\tilde{J}_c = \sum_j \mu_j N_j - \sum_k (p^k - p)V^k + \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \quad (34)$$

$$d\tilde{J}_c = -SdT - \sum_i N_i d\mu_i + \sum_j \mu_j dN_j + Vdp + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \quad (35)$$

In the Gibbsian thermodynamics of capillary systems, surface and line excess values of thermodynamic potentials are also introduced. However, in the definition expressed in Equation (24), the second term is a bulk quantity, the surface excess of which is equal to zero. Therefore, we can conclude that the surface excess of the J -potential is always equal to the surface excess of the grand thermodynamic potential;¹³ the same applies to the line excesses:

$$\bar{J} = \bar{\Omega} = \gamma A, \quad \bar{\bar{J}} = \bar{\bar{\Omega}} = \tau L. \quad (36)$$

The overline here denotes the surface excess quantities, and the double overline the corresponding line excesses.

The foregoing is quite enough for the first acquaintance with the J -potential. Here we turn to an example of using the J -potential in a theoretical study.

3. Dependence of the chemical potential of a gas in a bubble on the bubble size

3.1 Conditions for equilibrium and stability

Let us consider a single-component two-phase (phases α and β) system with a curved interface. Phase α (more

precisely, the equilibrium nucleus of this phase) is a vapor bubble (see Figure 1), obviously located on the concave side of the interface. The equilibrium and stability conditions can be derived using any thermodynamic potential, but in our case, the simplest of them is the J -potential, which we define as

$$J_c \equiv \Omega + p^\beta V, \quad (37)$$

where Ω is the grand thermodynamic potential and $V = V^\alpha + V^\beta$ is the total volume of the system. Obviously, Equation (37) corresponds to the definition expressed in Equation (24) when p^β is chosen as the external pressure. Thus, we are dealing with the classical J -potential J_c . The work of formation of an equilibrium spherical nucleus of the phase α in the phase β will be found as the difference between the J -potential for homogeneous ($V^\alpha = 0$) and heterogeneous states, but, since for a homogeneous state $J_c = 0$, this work is simply equal to the value J_c for a heterogeneous state

$$J_c = -(p^\alpha - p^\beta)V^\alpha + \gamma A, \quad (38)$$

where γ is the surface tension of the bubble, referred to the surface of tension as a dividing surface, and A is the area of this surface ($V^\alpha = 4\pi R^3/3$ and $A = 4\pi R^2$ with R the radius of the surface of tension).

As applied to the J -potential of our system, the Gibbs equilibrium principle is formulated as

$$(\delta J_c)_{T, p^\beta} = 0 \quad \text{or} \quad (\delta J_c)_{T, \mu} = 0. \quad (39)$$

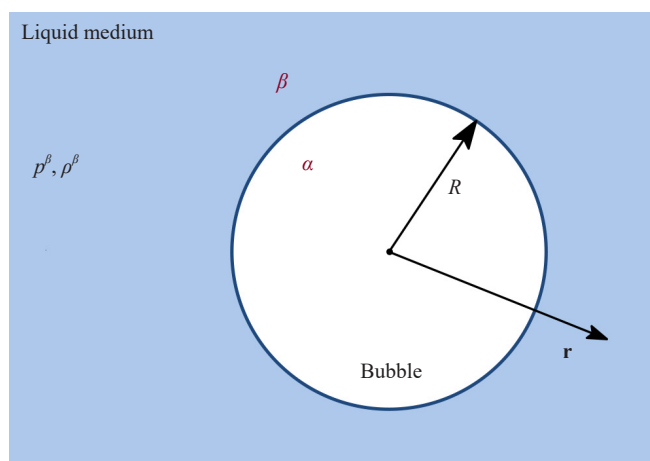


Figure 1. A schematic representation of a vapor bubble (a critical nucleus of the vapor phase α) formed in the bulk liquid phase β . The values of the temperature T and the pressure p^β in the liquid phase (or the chemical potential μ) are fixed. The radius R corresponds to the surface of tension chosen as the bubble–liquid dividing surface. The radius-vector \mathbf{r} defines a specific point when the system is considered as a continuous inhomogeneous fluid (in Sec. 3.2)

These conditions are equivalent, since only two variables out of these three can be chosen as independent, the third one can be found from the Gibbs–Duhem equation for the phase β :

$$-s^\beta dT + dp^\beta - \rho^\beta d\mu = 0, \quad (40)$$

with $s^\beta \equiv S^\beta/V^\beta$ the bulk density of the entropy and $\rho^\beta \equiv N^\beta/V^\beta$ the number density of molecules in the phase β .

With the indicated fixings, the quantities $p^{\alpha, \beta}$ and γ for the surface of tension will also be constant (each of them can be set by setting the values of the temperature T and the chemical potential μ), and therefore the substitution of Equation (38) into any of Equations (39) gives

$$-(p^\alpha - p^\beta)dV^\alpha + \gamma dA = 0. \quad (41)$$

From this, we obtain the condition

$$p^\alpha - p^\beta = \frac{2\gamma}{R}, \quad (42)$$

which is nothing but the Laplace equation and determines the size of the equilibrium nucleus. To find out the type of equilibrium, we need to differentiate Equation (38) again and substitute Equation (42) into it:

$$\left(\frac{\partial^2 J}{\partial R^2}\right)_{T, p^\beta} \equiv \left(\frac{\partial^2 J}{\partial R^2}\right)_{T, \mu} = -(p^\alpha - p^\beta) \left(\frac{\partial^2 V^\alpha}{\partial R^2}\right)_{T, p^\alpha} + \gamma \left(\frac{\partial^2 A}{\partial R^2}\right)_{T, p^\alpha} = -8\pi\gamma. \quad (43)$$

The negative value of the second derivative corresponds to the maximum of the J -potential, which means that the equilibrium of the vapor phase nucleus with the liquid in an open system is unstable. This fact underlies the classical theory of nucleation. Substitution of Equation (42) into Equation (38) leads to the Gibbs formula for the work of formation of a critical nucleus

$$J_c = \gamma A/3. \quad (44)$$

3.2 Finding the dependence of the chemical potential on the bubble radius at a constant temperature

Our system has two degrees of freedom (since it is single-component and contains two phases), and, therefore, when the temperature is fixed, there must be an unambiguous dependence of the chemical potential μ of the molecules of the fluid on the bubble radius R . Let us find it. Obviously, R can only be taken from the Laplace equation (42), and therefore we will proceed, writing it in differential form:

$$dp^\alpha - dp^\beta = \frac{2}{R} d\gamma - \frac{2\gamma}{R^2} dR. \quad (45)$$

Now we write the isothermal Gibbs–Duhem equation for the phases α and β

$$dp^\alpha = \rho^\alpha d\mu, \quad dp^\beta = \rho^\beta d\mu, \quad (46)$$

and the Gibbs adsorption equation

$$d\gamma = -\Gamma d\mu. \quad (47)$$

Substitution of Equations (46) and (47) into Equation (45) gives

$$\frac{d\mu}{dR} = -\frac{2\gamma}{R^2(\rho^\alpha - \rho^\beta + 2\Gamma/R)}. \quad (48)$$

Finally, recall Tolman's formula¹⁷

$$\frac{\Gamma}{\rho^\alpha - \rho^\beta} = \delta \left[1 + \frac{\delta}{R} + \frac{1}{3} \left(\frac{\delta}{R} \right)^2 \right], \quad (49)$$

where $\delta \equiv R' - R$ is the Tolman length and R' is the radius of the equimolecular surface, i.e. the surface of zero adsorption Γ). Using Equation (49), we reduce (48) to the form

$$\frac{d\mu}{dR} = -\frac{2\gamma}{R^2(\rho^\alpha - \rho^\beta) \left[1 + \frac{2\delta}{R} + \frac{2\delta^2}{R^2} + \frac{2\delta^3}{3R^3} \right]} \quad \text{or} \quad \frac{dR}{d\mu} = -\frac{R^2(\rho^\alpha - \rho^\beta)}{\gamma} \left[\frac{1}{2} + \frac{\delta}{R} + \frac{\delta^2}{R^2} + \frac{\delta^3}{3R^3} \right]. \quad (50)$$

Equations (50) are a rigorous solution to the problem. It can be seen that, for $R \gg |\delta|$, the sign of the derivative is determined by the difference $\rho^\alpha - \rho^\beta$. For drops ($\rho^\alpha > \rho^\beta$) we obtain $d\mu/dR < 0$, while for bubbles ($\rho^\alpha < \rho^\beta$) we obtain $d\mu/dR > 0$. Thus, in accordance with Equation (43), the unstable equilibrium of a drop corresponds to the roots of the equation $\mu = \mu^\beta$ lying on the descending curve, and in the case of a bubble, on the ascending curve. It is curious that even at $R = \delta$, the expression in square brackets remains positive regardless of the sign of the Tolman length δ , and, therefore, the indicated regularity remains in force.

Integration of (50) can be carried out with a known dependence of the densities ρ^α and ρ^β on μ , the Tolman length δ and surface tension γ on R . In particular, such dependencies can be constructed using asymptotic expansions in the small curvature parameter $\delta/R \ll 1$ and the small parameter $2\gamma\chi^\beta/R \ll 1$ associated with the isothermal compressibility χ^β of the fluid. If we use the ideal gas approximation for vapor in a bubble, then, in the leading order in small parameters δ/R and $2\gamma\chi^\beta/R$, the radius R is related to the chemical potential μ as

$$R = \frac{2\gamma}{p_\infty \left(e^{\Delta\mu/k_B T} - 1 \right) - \rho^\beta \Delta\mu}, \quad (51)$$

where $\Delta\mu \equiv \mu - \mu_\infty$, μ_∞ and p_∞ are the chemical potential of the substance and, accordingly, the pressure at equilibrium of the liquid and gas phases with a flat interface (i.e., at the liquid–gas binodal), k_B is the Boltzmann constant. It is easy to verify by differentiating Equation (51) with respect to R that Equation (51) corresponds to the second of Equations (50) in the leading order in small parameters and in the ideal gas approximation for vapor in the bubble.

Within the framework of statistical thermodynamics, the complete dependence of the chemical potential of a substance in a bubble on the radius of the dividing surface for very small drops, for which the parameters δ/R and $2\gamma\chi^\beta/R$ are no longer small, can be constructed using the gradient¹⁸ or integral^{19,20} density functional theory. In particular, within the framework of the gradient Density Functional Theory (DFT), the grand thermodynamic potential for a heterogeneous liquid–bubble system, neglecting correlations of hard spheres, can be represented^{18,21,22} as a functional of the local number density of molecules $\rho(\mathbf{r})$:

$$\Omega[\rho(\mathbf{r})] = \int_{(V)} \left\{ f_{\text{hs}}(\rho(\mathbf{r})) - a\rho^2(\mathbf{r}) + \frac{C}{2}(\nabla\rho(\mathbf{r}))^2 - \mu\rho(\mathbf{r}) \right\} d\mathbf{r}, \quad (52)$$

where (V) denotes, as the range of integration, the whole volume occupied by the fluid, $f_{\text{hs}}(\rho(\mathbf{r}))$ is the free energy density of a homogeneous system of hard spheres with number density $\rho(\mathbf{r})$ at a point \mathbf{r} relative to the bubble center (see Figure 1), $a = -\frac{1}{2} \int_V d\mathbf{r} w(\mathbf{r})$ is the mean-field parameter determined by the long-range intermolecular attraction potential $w(r)$, $C = -\frac{2}{3} \pi \int_0^\infty dr r^4 w(r)$, and $\nabla\rho(\mathbf{r})$ is the gradient of the number density of molecules.

Taking into account definition expressed in Equation (38) and expression (52), we can now represent the classical J -potential in the form of a local density functional of $\rho(\mathbf{r})$ as

$$J_c[\rho(\mathbf{r})] = \int_{(V)} \left\{ f_{\text{hs}}(\rho(\mathbf{r})) - a\rho^2(\mathbf{r}) + \frac{C}{2}(\nabla\rho(\mathbf{r}))^2 - \mu\rho(\mathbf{r}) + p^\beta \right\} d\mathbf{r}. \quad (53)$$

The Gibbs equilibrium principle (39), when Equation (53) is varied with respect to the local density $\rho(\mathbf{r})$, now leads to a differential equation (the Euler–Lagrange equation for the functional (53)) for the spherically-symmetric equilibrium density profile $\rho^{(e)}(r)$:

$$-\frac{C}{r^2} \frac{d}{dr} \left(r^2 \frac{d\rho^{(e)}}{dr} \right) + \mu_{\text{hs}}(\rho^{(e)}(r)) - 2a\rho^{(e)} = \mu \quad (54)$$

with $\mu_{\text{hs}}(\rho^{(e)}(r))$ the chemical potential of a homogeneous system of hard spheres with number density $\rho^{(e)}(r)$.

The dependence $\mu_{\text{hs}}(\rho^{(e)}(r))$ can be determined using the Carnahan–Starling²³ (or another suitable¹⁹) equation of state for a system of hard spheres. Then, the differential equation (54) with respect to the equilibrium profile $\rho^{(e)}(r)$ can be solved numerically with boundary conditions $d\rho^{(e)}/dr|_{r=0} = 0$ and $\rho^{(e)}|_{r \rightarrow \infty} = \rho^\beta(\mu)$, e.g. by the shooting method²⁴ at each given value of the chemical potential μ . By substituting the found profile into Equation (53), at the next step, we find the value of the potential J_c for the given μ . According to Equation (43), the obtained value $J_c(\mu)$ for an open system corresponds to a saddle point in the functional space of density profiles. If we then choose the surface of tension as the dividing surface for the bubble, taking into account Equations (42) and (44), we find

$$\gamma(\mu) = \left(\frac{3J_c(\mu)(p^\alpha(\mu) - p^\beta(\mu))^2}{16\pi} \right)^{1/3}, \quad R(\mu) = 2 \left(\frac{3J_c(\mu)}{16\pi(p^\alpha(\mu) - p^\beta(\mu))} \right)^{1/3}. \quad (55)$$

Here, the pressures $p^{\alpha,\beta}(\mu)$ in the phases are determined using the co-relations

$$p^{\alpha,\beta}(\mu) = -f_{\text{hs}}(\rho^{\alpha,\beta}(\mu)) + a(\rho^{\alpha,\beta}(\mu))^2 + \mu\rho^{\alpha,\beta}(\mu), \quad (56)$$

arising from Equation (52) or (53) applied to homogeneous densities in bulk α and β phases, and the corresponding volumetric densities $\rho^{\alpha,\beta}(\mu)$ as solutions of the transcendental equations

$$\mu_{\text{hs}}(\rho^{\alpha,\beta}(\mu)) - 2a\rho^{\alpha,\beta}(\mu) = \mu, \quad (57)$$

following from Equation (54). It can be easily seen from Equation (56), that the integral (53) does not have such a divergence at an infinite increase of the system size as the integral (52): the asymptotic value $\rho^{(e)}(r)|_{r \rightarrow \infty} = \rho^\beta(\mu)$ of the density satisfying Equation (57) makes the asymptotic value of the integrand in (53) zero. This property of the classical J -potential is expected, since it equals zero in the bulk liquid phase β .

Thus, expressions (55) solve the problem of finding the complete relationship between the chemical potential μ of a substance in a bubble on the radius R of the surface of tension and, in addition, determine the dependence of the surface tension γ (calculated for the surface of tension) of a small vapor bubble on μ and R . This problem was previously solved by choosing the equimolecular surface of radius R' as the dividing surface for a bubble in stretched liquid argon.¹⁸

A similar approach, including the consideration of the J -potential as a functional of the local density of matter, can be developed in the case of homogeneous formation of drops or bubbles in a closed system²⁵ and in the case of heterogeneous formation of a droplet or bubble around a spherical solid particle in an open²⁶⁻²⁸ or closed²⁹ system. In contrast to the considered case, in which only unstable equilibrium nuclei of the new phase corresponding to the maximum/saddle point of the J -potential are possible, in the latter cases, the minimum (stable nucleus) and maximum/saddle point (unstable nucleus) of the J -potential can coexist simultaneously.

4. Conclusion

We have considered the J -potential introduced earlier^{12,13,15} by one of us (A.I.R.) as another one in the series of thermodynamic potentials. It can be generally defined by Equation (24) as the grand thermodynamic potential plus the volume of the system multiplied by some pressure p' (which may be the external pressure, the pressure in one of the phases in a multiphase system). We have also considered the variants of the J -potential: the classical one, J_c , (when p' is chosen equal to the pressure in one of the phases in the system) and the hybrid one, \tilde{J} (when the hybrid potential $\tilde{\Omega}$ is taken instead of the grand potential Ω in the definition (24)). The classical J -potential turns to zero in a bulk homogeneous fluid, but it can be conveniently used in heterogeneous/multicomponent systems when the temperature and one of the pressures are set. The surface and line excesses of the J -potential are equal to the corresponding excesses of the grand potential Ω and, thus, their values per unit area of the interface/unit length of the interfacial contact line yield the surface/line tension.

We have considered the use of the classical J -potential for the thermodynamic analysis of the formation of a vapor bubble in a metastable (stretched or superheated) bulk single-component liquid. Since it turns to zero in the bulk liquid phase, its value naturally does not depend on the total volume of the system and yields the work of formation of the critical bubble. The functional of the classical J -potential used in the density functional theory inherits this property of the classical J -potential: it remains finite for the system with a bubble at an infinite increase of the system size, which is an obvious advantage of using this potential. At the same time, it allows one to use the techniques for solving the problems developed for the functionals of the grand potential.

Conflicts of interest

The authors declare no conflict of interest.

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