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New Thermodynamic Potential in Classical Thermodynamics

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Abstract: The article introduces the reader to the new thermodynamic potential of classical thermodynamics, called the *J*-potential. For the case of a homogeneous system, it vanishes, but it perfectly serves multiphase (heterogeneous) systems. The *J*-potential is especially important for the thermodynamics of capillary systems in colloid science. The *J*-potential has found applications in thermodynamics of thin films, simple derivation of the Neumann and Young equations, and theory of strength of materials. In this work, for example, it is used to study the dependence of the chemical potential of a substance in a small bubble on the bubble size.

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

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 the process using thermodynamic potentials is very simple: changing the thermodynamic potential under certain conditions is this work. 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 assume that the state of matter is fluid and we 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

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

with S as the entropy of the system, T the absolute temperature, A the area of the surface, $\mathbf{P}$ the local vector of the external force (called stress) applied to the unit of the external surface of the system, $\mathbf{u}$ the local displacement vector of the system surface. The scalar product $\mathbf{P}\cdot\delta\mathbf{u}$ gives the elementary work of displacement of a unit surface. 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 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 as 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 system with external bodies. Equation (1) implies the condition

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

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. Free energy (adding the word "Helmholtz" is no longer accepted) F is defined as

$$F \equiv U - TS. \tag{3}$$

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

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

and it follows from Equation (4)

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

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, 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:

$$G \equiv F + pV \equiv U - TS + pV. \tag{6}$$

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

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

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

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

From here, the condition follows

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

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's move on to the enthalpy *H*. This value 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's find these conditions. The definition of enthalpy is known only for a system in a medium with constant pressure *p*:

$$H \equiv U + pV\,. \tag{10}$$

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

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

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

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

from which it follows

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

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 a grand canonical distribution. For it there is a strict definition

$$\Omega \equiv U - TS - \sum_i \mu_i N_i \equiv F - \sum_i \mu_i N_i\,. \tag{14}$$

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

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

From here, it follows

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

Equation (16) indicates that Ω works as a grand thermodynamic potential at constant temperature, displacement vector of the system boundary 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

$$U = TS - pV + \sum_i \mu_i N_i\,, \tag{17}$$

$$F = -pV + \sum_i \mu_i N_i\,, \tag{18}$$

$$G = \sum_i \mu_i N_i\,, \tag{19}$$

$$H = TS + \sum_i \mu_i N_i \,, \tag{20}$$

$$\Omega = -pV. \tag{21}$$

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. 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 whole sum, but only some terms of the sum can be subtracted. 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

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

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 a grand thermodynamic potential with respect to the components of group *k* (such thermodynamic potentials are called hybrid). 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. In particular, it is important for mechanochemistry.

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 a grand thermodynamic potential (21) in this case takes the form

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

and from here it is quite possible to subtract $-pV$. In this way, a new thermodynamic potential was introduced, called the *J*-potential [3,4]. 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.

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 in Ref. [5], 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:

$$J \equiv \Omega + p'V \tag{24}$$

with *V* as the volume of the system, and there is some pressure p' 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 real 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 written in the form

$$\Omega = -\sum_k p^k V^k + \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \tag{25}$$

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

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

where the obvious relation has been taken into account

$$V = \sum_k V^k. \tag{27}$$

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

$$d\Omega = -SdT - \sum_i N_i d\mu_i - pdV + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \tag{28}$$

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

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

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

$$dJ_{\mathrm{c}} = -SdT - \sum_i N_i d\mu_i + Vdp + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \tag{30}$$

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

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

Let us now introduce the hybrid *J*-potential (the notation is $\tilde{J}$). 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):

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

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

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

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

$$d\tilde{J}_{\mathrm{c}} = -SdT - \sum_i N_i d\mu_i + \sum_j \mu_j dN_j + Vdp + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t. \tag{35}$$

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 a grand thermodynamic potential [4]:

$$\overline{J} = \overline{\Omega} = \gamma A, \tag{36}$$

where the overline means the surface excess. The problem is solved similarly with line excesses (denoted by two lines above):

$$\overline{\overline{J}} = \overline{\overline{\Omega}} = \tau L. \tag{37}$$

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 one-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, 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

$$J \equiv \Omega + p^{\beta} V, \tag{38}$$

where Ω is the grand thermodynamic potential and $V = V^{\alpha} + V^{\beta}$ is the total volume of the system. Obviously, Equation (38) 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 $J_{\mathrm{c}} = 0$, this work is simply equal to the value J_{c} for a heterogeneous state

$$J_{\mathrm{c}} = -(p^{\alpha} - p^{\beta}) V^{\alpha} + \gamma A, \tag{39}$$

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

$$(\delta J_{\mathrm{c}})_{T,\mu,p^{\beta}} = 0. \tag{40}$$

With the indicated fixings, the quantities p^{α} and γ for the surface of tension will also be constant, and therefore the substitution of Equation (39) into Equation (40) gives

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

From this we obtain the condition

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

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 (39) again and substitute Equation (42) into it:

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

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 (39) leads to the Gibbs formula for the work of formation of a critical nucleus

$$J_{\mathrm{c}} = \gamma A/3. \tag{44}$$

3.2. *Finding the Dependence of μ on R at a Constant Temperature*

Our system has $n + 1 = 2$ degrees of freedom, and, therefore, when the temperature is fixed, there must be an unambiguous dependence of μ on R. Let's find it. Obviously, R can only be taken from the Laplace equation, and therefore we will proceed from Equation (42), writing it in differential form:

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

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

$$dp^{\alpha} = \rho^{\alpha} d\mu, \quad dp^{\beta} = \rho^{\beta} d\mu \tag{46}$$

and the Gibbs adsorption equation

$$d\gamma = -\Gamma d\mu . \tag{47}$$

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

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

Finally, recall Tolman's formula

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

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

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

or

$$\frac{dR}{d\mu} = -\frac{R^2(\rho^{\alpha} - \rho^{\beta})}{\gamma}\left[\frac{1}{2} + \frac{\delta}{R} + \frac{\delta^2}{R^2} + \frac{\delta^3}{3R^3}\right]. \tag{51}$$

Equations (50) and (51) are a rigorous solution of 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 $(\rho^{\alpha} > \rho^{\beta})$ $d\mu/dR < 0$ and for bubbles $(\rho^{\alpha} < \rho^{\beta})$ $d\mu/dR > 0$. 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 δ, and, therefore, the indicated regularity remains in force.

Integration of (50) or (51) 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 compressibility of the fluid χ^{β}. If we use the ideal gas approximation for vapor in a bubble, then, in the leading order in small parameters $\delta/R \ll 1$ and $2\gamma\chi^{\beta}/R \ll 1$, the radius R is related to the chemical potential μ by the relation

$$R = \frac{2\gamma}{p_{\infty}\left(e^{\Delta\mu/k_B T} - 1\right) - \rho^{\beta}\Delta\mu} , \tag{52}$$

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. It is easy to verify by differentiating Equation (52) with respect to *R* that Equation (52) corresponds to Equation (51) 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 and are no longer small, can be constructed using the gradient [6] or integral [7,8] density functional theory. In particular, within the framework of the gradient density functional theory, the grand thermodynamic potential for a heterogeneous liquid–bubble system, neglecting correlations of hard spheres, can be represented [6,9,10] as a functional of the local density of the number of molecules $\rho(\vec{r})$:

$$\Omega = \int_V \left\{ f_{\text{hs}}\left[\rho(\vec{r})\right] - a\rho^2(\vec{r}) + \frac{C}{2}\left(\nabla\rho(\vec{r})\right)^2 - \mu\rho(\vec{r}) \right\} d\vec{r}\,, \tag{53}$$

where V is the volume of the system, $f_{\text{hs}}\left[\rho(\vec{r})\right]$ is the free energy density of hard spheres at a point $\vec{r}$ relative to the bubble center, the factor $a = -\frac{1}{2}\int_V d\vec{r}\, w(\vec{r}) \;\; = -2\pi\int_0^\infty dr\, r^2 w(r)$ is the mean-field parameter determined by the long-range intermolecular attraction potential $w(\vec{r})$, $C = -\frac{2}{3}\pi\int_0^\infty dr\, r^4 w(r)$, $\nabla\rho(\vec{r})$ is the density gradient of the number of molecules.

Taking into account definition expressed in Equation (38) and relation (53), we can now represent the classical *J*-potential in the form of a local density functional $\rho(\vec{r})$ as

$$J_c = \int_V \left\{ f_{\text{hs}}\left[\rho(\vec{r})\right] - a\rho^2(\vec{r}) + \frac{C}{2}\left(\nabla\rho(\vec{r})\right)^2 - \mu\rho(\vec{r}) + p^\beta \right\} d\vec{r}\,. \tag{54}$$

The Gibbs equilibrium principle $(\delta J_{\text{c}})_{T,\mu,p^\beta} = 0$, when Equation (54) is varied with respect to the local density $\rho(\vec{r})$, now leads to a differential equation for the equilibrium density profile $\rho^{(\text{e})}(\vec{r})$:

$$-\frac{C}{r^2}\frac{d}{dr}\left(r^2 \frac{d\rho^{(\text{e})}}{dr} \right) + \mu_{\text{hs}}\left(\rho^{(\text{e})}(\vec{r})\right) - a\rho^{(\text{e})} = \mu\,, \tag{55}$$

where $\mu_{\text{hs}}\left(\rho^{(\text{e})}(\vec{r})\right)$ is the chemical potential of a system of hard spheres with density $\rho^{(\text{e})}(\vec{r})$.

The dependence $\mu_{\text{hs}}\left(\rho^{(\text{e})}(\vec{r})\right)$ can be determined using the Carnahan-Starling (or another suitable [7]) equation of state for a system of hard spheres. Then, the differential equation (55) with respect to the equilibrium profile $\rho^{(\text{e})}(\vec{r})$ can be solved numerically by the shooting method at each given value of the chemical potential μ. By substituting the found profile into Equation (54), at the next step, we find the value of the potential J_{c} for the given μ. According to Equation (43), the obtained value $J_{\text{c}}(\mu)$ for an open system corresponds to a saddle point in the functional space of density profiles. If we choose the surface of tension as the dividing surface for the bubble, then, taking into account Equations (42) and (44), we find

$$\gamma(\mu) = \left(\frac{3J_{\text{c}}(\mu)\left(p^\alpha(\mu) - p^\beta(\mu)\right)^2}{16\pi} \right)^{1/3}, \tag{56}$$

$$R(\mu) = 2\left(\frac{3J_c(\mu)}{16\pi\left(p^\alpha(\mu) - p^\beta(\mu)\right)} \right)^{1/3}. \tag{57}$$

Here, the pressures $p^{\alpha,\beta}(\mu)$ in the phases are determined using the co-relations arising from Equation (53) $p^{\alpha,\beta}(\mu) = -f_{\text{hs}}\left[\rho^{\alpha,\beta}(\mu)\right] + a\left(\rho^{\alpha,\beta}(\mu)\right)^2 + \mu\rho^{\alpha,\beta}(\mu)$, and the corresponding volumetric densities $\rho^{\alpha,\beta}(\mu)$ as solutions of the transcendental equations $\mu_{\text{hs}}\left(\rho^{\alpha,\beta}(\mu)\right)-2a\rho^{\alpha,\beta}(\mu)=\mu$ following from Equation (55). Thus, expressions (56) and (57) 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 (for the surface of tension) of a small vapor bubble on μ and R. In Ref. [6], this problem was solved by choosing the equimolecular surface of radius R' as a dividing surface for a bubble in stretched liquid argon.

In conclusion, we note that we have considered the use of the *J*-potential for the thermodynamic analysis of the homogeneous formation of a vapor bubble in a stretched or superheated bulk liquid. 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 system [11] and in the case of heterogeneous formation of a droplet or bubble around a spherical solid core in an open system [12–14]. 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 these cases, the minimum (stable nucleus) and maximum/saddle point (unstable nucleus) of the *J*-potential can coexist simultaneously.

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References

1. The Scientific Papers of J. Willard Gibbs in Two Volumes. Vol. 1. Thermodynamics. Vol. 2. Statistical Mechanics. Longmans, Green and Co. London, New York and Bombay, 1906.
2. The Collected Works of J. Willard Gibbs in Two Volumes. Vol. 1. Thermodynamics. Vol. 2. Statistical Mechanics. Longmans, Green and Co. London, New York and Bombay, 1928, 1931, 1948.
3. Rusanov, A.I. One more important thermodynamic potential for solids and heterogeneous systems. *J. Chem. Phys*. **2013**, *138*, 246101.
4. Rusanov, A.I. New thermodynamic potentials for surface science. *Colloids Surf. A* **2014**, *443*, 363–367.
5. Rusanov, A.I. On thermodynamics of thin films. *J*-potential. *Colloid J*., **2020**, *82*, 54–61.
6. Shchekin, A.K., Gosteva, L.A., Lebedev,a T.S. Thermodynamic properties of stable and unstable vapor shells around lyophobic nanoparticles. *Physica A* **2020**, *560,* 125105.
7. Shchekin, A.K., Tatyanenko, D.V., Gosteva, L.A., and Apitsin, K.D. On the Choice of the Equation of State for a System of Hard Spheres in Calculations of Density Profiles and Surface Tension of Droplets and Bubbles. *Rus. J. Gen. Chem*. **2022**, *92*, 629–640.
8. Evans, R. The Nature of the Liquid-Vapour Interface and Other Topics in The Statistical Mechanics of Non-Uniform, Classical Fluids, *Advances in Physics* **1979**, *28*, 143–200.
9. Lu, B.Q., Evans, R., Telo da Gama, M.M. The Form of the Density Profile at a Liquid-Gas Interface. *Mol. Phys.* **1985**, *55*, 1319−1338.
10. Gosteva L.A., Shchekin A.K. Calculations of Thermodynamic Characteristics of Vapor Interlayers with the Use of Gradient and Integral Density Functional Theories and Nudged Elastic Band Method, *Colloid J.* **2021**, *83*, 558----565.
11. Shchekin, A.K., Volkov, N.A., Koga, K. The Effect of a Finite Number of Monomers Available for Aggregation at Nucleation and Micellization in a Fixed Volume, *J. Chem.* **2019**, *151*, 244903.
12. Shchekin, A.K. Thermodynamically Stable Nanodroplets and Nanobubbles. *Russ. Chem. Bull.* **2023,** *72*, 295–311.
13. Shchekin, A.K., Lebedeva, T.S., Tatyanenko, D.V. Key Thermodynamic Characteristics of Nucleation on Charged and Neutral Cores of Molecular Sizes in Terms of the Gradient Density Functional Theory, *Colloid J.* **2016**, *78*, 553–565.
14. Shchekin, A.K., Lebedeva, T.S. Density functional description of size-dependent effects at nucleation on neutral and charged nanoparticles, *J. Chem. Phys.***2017**, *146*, 094702.