New Approach to Defining Thermodynamic Surface Tension of Solids

A. I. Rusanov[a], D. V. Tatyanenko[b], and A. K. Shchekin[b]

[a] *Mendeleev Center, St. Petersburg State University, Universitetskaya nab. 5/7, St. Petersburg, 199034 Russia*
[b] *Fock Research Institute of Physics, Theoretical Physics Department, St. Petersburg State University,*
ul. Ul'yanovskaya 1, Petrodvorets, St. Petersburg, 198504 Russia

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Abstract—Using either the chemical potential of the immobile component of a solid dissolved in a fluid phase or the corresponding component of the tensor of chemical potential in solid phase, a new concept of the grand thermodynamic potential of solid–fluid two-phase system is proposed. For a planar interfacial surface, this makes it possible to generalize the notion of thermodynamic surface tension σ introduced by Gibbs that has the meaning of the formation work of a unit surface. This tension is determined as the specific surface excess of the grand thermodynamic potential. This definition of the thermodynamic surface tension does not depend on the position of the dividing surface and is common for fluids and solids. It is shown that, at the arbitrary position of dividing surface, the difference between thermodynamic σ and mechanical γ surface tensions for solid surface is determined by the nonuniformity of the tensor of chemical potential in a solid, as well as by its anisotropy in the bulk of solid phase.

INTRODUCTION

In contrast to thermodynamics of fluid interfacial surfaces, the thermodynamics of the surface of solid becomes increasingly complicated in its development. The tensor nature of chemical potential of immobile component of the crystalline lattice, its principal non-uniformity (due to impossibility of diffusion) clearly distinguishes between the thermodynamics of both bulk solid and its surface and more simple thermodynamics of fluids [1–3]. In particular, there is a difference between thermodynamic surface tension σ (the formation work of the unit new surface) introduced by Gibbs [4] and mechanical surface tension γ (the tangential component of the specific surface excess of stress tensor, which is also called surface stress). For fluid interface, these values coincide in the absence of external fields [5, 6].

When describing surface layers according to the Gibbs approach, the properties of bulk phases are extended to a formally introduced dividing surface. The formed excesses of extensive thermodynamic quantities are referred to this surface. To some extent, the position of the dividing surface can be chosen arbitrarily. The choice is determined by simplicity of derived equations or the peculiarities of the considered system. In the case of the surface of solid, the natural choice is its boundary surface, which is set with accuracy to fractions of the interatomic distance. For a single-component solid, this surface can practically be described as an equimolecular surface with respect to the component of solid; i.e., such surface on which the adsorption (specific surface excess of matter) of the component of solid is equal to zero. This simplifies a

number of equations. In particular, when choosing an equimolecular dividing surface in a single-component system, thermodynamic surface tension σ is equal to specific surface free energy.

However, in the case of a multicomponent solid, an equimolecular surface with respect to one of the components will no longer have the same clear physical meaning. In addition, in a number of problems, it seems to be more convenient to choose another solid–fluid dividing surface. For example, when considering small sessile droplets, it is convenient to shift the dividing surface by the thickness of adsorption or wetting film formed on the surface of solid substrate [7, 8]; this thickness depends on the thermodynamic state of a system. Upon the arbitrary choice of dividing surface, an additional term that includes adsorption appears in relations for excess quantities. In a multicomponent system, this contribution includes the adsorptions of all components.

In a system composed of fluids, all components are mobile. To describe an open system with mobile components, it is convenient to use grand thermodynamic potential Ω defined as

$$\Omega \equiv F - \sum_i \mu_i N_i, \tag{1}$$

where F is the free energy of a system and μ_i and N_i are the chemical potential and the number of molecules of ith component in a system, respectively. The thermodynamic surface tension σ (in this case, it coincides with the mechanical surface tension γ) can be deter-

mined in a system such as the specific surface excess of grand thermodynamic potential as follows:

$$\sigma = \bar{\Omega}/A, \qquad (2)$$

where the bar denotes surface excess and A is the surface area of dividing surface. It is known that, for a planar fluid interface, this quantity does not depend on the position of dividing surface; i.e., this definition is true for an arbitrary position of dividing surface.

Since the chemical potential of the immobile component of the solid, a tensorial quantity, is not fixed in the grand canonical ensemble, the grand thermodynamic potential seems to be inapplicable to solids. Nevertheless, its use in the consideration of open heterogeneous systems that include both fluid phases and solids is a common practice. For example, hybrid potential $\tilde{\Omega}$ defined by the same formula (2), albeit with index i referred only to mobile components of the system, was introduced in [9]. This definition means that potential $\tilde{\Omega}$ behaves as the free energy with respect to immobile components (in solids) and as the grand thermodynamic potential with respect to mobile components (both in fluids and solids). The thermodynamic surface tension can be defined as the specific surface excess of hybrid potential $\tilde{\Omega}$ [1–3]; however, this is only true for the particular dividing surface. If we confine ourselves to the use of only this fixed dividing surface, as a rule, the hybrid potential is sufficient to consider two- and three-phase systems containing solids (e.g., it was applied for a system consisting of a solid substrate and a small sessile droplet in contact with vapor [10]).

In this work, we developed an alternative approach based on the use of the grand thermodynamic potential defined for solid using all its components [11]. This leads to a more general consideration including the shift of dividing surface and universal definition of quantity σ valid for an arbitrary position of the dividing surface.

Gibbs did not consider the dependence of the thermodynamic surface tension of a solid on the position of dividing surface and confined himself to the case of a single-component solid and the dividing surface that is equimolecular with respect to the component of solid ([4], p. 314). This problem was hardly raised in the literature with regard to the Gibbs dividing surface approach used in this work. This problem has been only recently touched upon in [12] devoted to line tension. The Gibbs approach was also recently generalized by Cammarata for solid–fluid interfaces in the multicomponent system [13] with use of thermodynamic potentials, which exclude the chemical potential of the immobile component from fundamental equations.

There is also an approach in which the surface layer between two phases was separated from each of the bulk phases by its own dividing surface. In this case, the values of thermodynamic quantities of the layer are associated with those of corresponding surface quantities. Within this approach, problems related to the difference between mechanically and thermodynamically defined surface tensions, which are close to problems treated in this work, have been discussed by Eriksson for the flat surface of a uniicomponent solid in contact with adsorbing gas [14].

GRAND THERMODYNAMIC POTENTIAL OF A BULK SOLID PHASE

Suggesting the presence of only one immobile component j (that is not principal constraint), we can write fundamental equations for the hybrid thermodynamic potential $\tilde{\Omega}$ of a solid phase as follows [1–3]:

$$d\tilde{\Omega} = -SdT + \hat{E} : d\hat{V} + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i, \qquad (3)$$

$$\tilde{\Omega} = E_{xx}V + \mu_{j(xx)}N_j, \qquad (4)$$

where S is the entropy; T is the temperature; $\hat{E}$ is the stress tensor; $\hat{V}$ is the volume displacement tensor [2, 3]; the colon denotes biscalar product of tensors [15]; $\hat{\mu}_j$ and $\hat{N}_j$ are the chemical potential and the mass displacement tensor of the immobile component, respectively; E_{xx} and $\mu_{j(xx)}$ are corresponding diagonal components of $\hat{E}$ and $\hat{\mu}_j$ tensors, respectively, for any direction x in which the solid phase is uniform; V is the volume per phase; and N_j is the number of molecules formed the crystalline lattice. The volume displacement tensor differs from the strain tensor in a trivial manner denoting the volume rather than linear changes at strain. Similarly, the mass displacement tensor indicates changes in mass at growth (or dissolution/evaporation) in different directions [2, 3]. Equality (4) is the result of the integration of Eq. (3) along chosen direction x at a fixed physical state.

In addition to the immobile component, a solid can also contain mobile components that move freely along the lattice. Gibbs called them fluid components (fluids absorbed by solids) and demonstrated that they behave similarly to a system composed of only fluids. Although the presence of these mobile components in a solid is unnecessary (and is not typical in practice), according to Gibbs, for generality, we assume that components of both types are present in solids. Speaking of solubility, we are first interested in the behavior of an immobile component, which can be either soluble or insoluble in the adjacent fluid.

Let us first consider the case when a solid (α phase) is in true equilibrium with a fluid β phase, in which this solid is partially soluble. The solid phase should be macroscopic, which allows one to consider a flat solid–fluid interface. Let us introduce Cartesian coordinates x, y, z with the z axis oriented along the normal to the interface toward the β phase. For simplicity, we suggest that shear stresses are absent in solid, so that

chosen coordinate axes coincide with principal directions of the stress tensor. This corresponds to the system considered by Gibbs ([4], p. 194), for which the equilibrium condition was derived as follows (Eq. (661) from [4]):

$$\left(f^{\alpha} - E_z^{\alpha} - \sum_i \mu_i^{\alpha} c_i^{\alpha}\right) \Big/ c_j^{\alpha} = \mu_j^{\beta}, \tag{5}$$

where f is the free energy density, E_z is the principal value of stress tensor $\hat{E}$ corresponding to direction z normal to the interface, and c is the concentration (the number of molecules per unit volume); subscripts i and j refer to mobile and immobile components, respectively. Upon the rigorous definition of the chemical potential tensor of immobile component of a solid, $\hat{\mu}_j^{\alpha}$ [1–3], the left-hand side of equality (5) can be identified with principal value $\mu_{j(z)}^{\alpha}$ of tensor $\hat{\mu}_j^{\alpha}$ that yields the equilibrium condition

$$\mu_{j(z)}^{\alpha} = \mu_j^{\beta}. \tag{6}$$

Furthermore, the condition for mechanical equilibrium

$$E_z^{\alpha} = -p^{\beta}, \tag{7}$$

where p^{β} is the hydrostatic pressure in fluid phase β, must be fulfilled.

In the considered situation, dissolved component j simultaneously plays the role of immobile (in phase α) and mobile (in phase β) components. Consequently, we can consider the chemical potential μ_j^{β} to be a variable of grand canonical ensemble (e.g., assuming that the system is in contact with a large reservoir of phase β). Let us define the grand thermodynamic potential of our two-phase system as

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_j^{\beta} N_j = \tilde{\Omega} - \mu_j^{\beta} N_j. \tag{8}$$

Applying this definition to uniform phases and taking into account expression (4), we arrive at the following relations:

$$\Omega^{\alpha} = E_k^{\alpha} V^{\alpha} + (\mu_{j(k)}^{\alpha} - \mu_j^{\beta}) N_j^{\alpha}, \ k = x, y, z, \tag{9}$$

$$\Omega^{\beta} = -p^{\beta} V^{\beta}, \tag{10}$$

or, passing to the density of grand thermodynamic potential $\omega \equiv \Omega / V$, at relations

$$\omega^{\alpha} = E_k^{\alpha} + (\mu_{j(k)}^{\alpha} - \mu_j^{\beta}) c_j^{\alpha}, \ k = x, y, z, \tag{11}$$

$$\omega^{\beta} = -p^{\beta}. \tag{12}$$

For the density of hybrid potential $\tilde{\omega} \equiv \tilde{\Omega} / V$, we obtain the following expressions:

$$\tilde{\omega}^{\alpha} = E_k^{\alpha} + \mu_{j(k)}^{\alpha} c_j^{\alpha}, \ k = x, y, z, \tag{13}$$

$$\tilde{\omega}^{\beta} = -p^{\beta} + \mu_j^{\beta} c_j^{\beta}. \tag{14}$$

Since energetic quantities ω^{α} and $\tilde{\omega}^{\alpha}$ cannot depend on the direction in the bulk phase, the right-hand sides of expressions (11) and (13) must be invariant with respect to the choice of principal direction. Thus, we arrive at the equalities

$$E_x^{\alpha} + \mu_{j(x)}^{\alpha} c_j^{\alpha} = E_y^{\alpha} + \mu_{j(y)}^{\alpha} c_j^{\alpha} = E_z^{\alpha} + \mu_{j(z)}^{\alpha} c_j^{\alpha}. \tag{15}$$

GRAND THERMODYNAMIC POTENTIAL OF THE SURFACE OF SOLID

Expressions shown above refer to a bulk phase. Passing to interfaces and introducing the local concentrations $c_j(z)$, the local densities of grand thermodynamic and hybrid potentials, $\omega(z)$ and $\tilde{\omega}(z)$, respectively, can be written by analogy with expressions (11) and (13) as

$$\omega(z) = E_k(z) + [\mu_{j(k)}(z) - \mu_j^{\beta}] c_j(z), \ k = x, y, \tag{16}$$

$$\tilde{\omega}(z) = E_k(z) + \mu_{j(k)}(z) c_j(z), \ k = x, y. \tag{17}$$

The $k = z$ case is automatically excluded in expressions (16) and (17) because integral thermodynamic relations can only be written for the directions in which the system is uniform, e.g., when passing from relation (3) to expression (4). In our case, the system is two-phase and uniform in directions x and y at any preset z, but nonuniform in direction z in the interfacial layer. To calculate excess quantities $\overline{\omega} \equiv \overline{\Omega} / A$ of grand thermodynamic and $\overline{\tilde{\omega}} \equiv \overline{\tilde{\Omega}} / A$ of hybrid potentials, we introduce a dividing surface at $z = z_0$, thus yielding the expressions

$$\overline{\omega} = \int_{-\infty}^{z_0} [\omega(z) - \omega^{\alpha}] dz + \int_{z_0}^{\infty} [\omega(z) - \omega^{\beta}] dz, \tag{18}$$

$$\overline{\tilde{\omega}} = \int_{-\infty}^{z_0} [\tilde{\omega}(z) - \tilde{\omega}^{\alpha}] dz + \int_{z_0}^{\infty} [\tilde{\omega}(z) - \tilde{\omega}^{\beta}] dz, \tag{19}$$

or, substituting expressions (11–17), we arrive at

$$\overline{\omega} = \gamma_k + \int_{-\infty}^{z_0} \left[\left(\mu_{j(k)}(z) - \mu_j^{\beta}\right) c_j(z) - \left(\mu_{j(k)}^{\alpha} - \mu_j^{\beta}\right) c_j^{\alpha}\right] dz$$
$$+ \int_{z_0}^{\infty} \left(\mu_{j(k)}(z) - \mu_j^{\beta}\right) c_j(z) dz, \ k = x, y, \tag{20}$$

$$\overline{\tilde{\omega}} = \gamma_k + \int_{-\infty}^{z_0} \left[\mu_{j(k)}(z) c_j(z) - \mu_{j(k)}^{\alpha} c_j^{\alpha}\right] dz$$
$$+ \int_{z_0}^{\infty} \left[\mu_{j(k)}(z) c_j(z) - \mu_j^{\beta} c_j^{\beta}\right] dz, \ k = x, y, \tag{21}$$

where

$$\gamma_k = \int\limits_{-\infty}^{z_0} \left(E_k - E_k^\alpha \right) dz + \int\limits_{z_0}^{\infty} \left(E_k + p^\beta \right) dz, \ k = x, y \quad (22)$$

are nothing more than the principal values of the two-dimensional tensor of mechanical surface tension.

Adding to and subtracting $\mu_{j(k)}^\alpha c_j(z)$ from the integrand in first integrals in formulas (20) and (21), we rewrite expressions (20) and (21) as follows:

$$\overline{\omega} = \gamma_k + \overline{g}_{j(k)} + \left(\mu_{j(k)}^\alpha - \mu_j^\beta \right) \Gamma_j^\alpha, \ k = x, y, \quad (23)$$

$$\overline{\overline{\omega}} = \gamma_k + \overline{g}_{j(k)} + \mu_{j(k)}^\alpha \Gamma_j^\alpha + \mu_j^\beta \Gamma_j^\beta, \ k = x, y, \quad (24)$$

where

$$\overline{g}_{j(k)} \equiv \int\limits_{-\infty}^{z_0} \left(\mu_{j(k)}(z) - \mu_{j(k)}^\alpha \right) c_j(z) dz +$$
$$\qquad (25)$$
$$+ \int\limits_{z_0}^{\infty} \left(\mu_{j(k)}(z) - \mu_j^\beta \right) c_j(z) dz, \ k = x, y,$$

and quantities

$$\Gamma_j^\alpha \equiv \int\limits_{-\infty}^{z_0} \left(c_j(z) - c_j^\alpha \right) dz, \ \Gamma_j^\beta \equiv \int\limits_{z_0}^{\infty} \left(c_j(z) - c_j^\beta \right) dz \quad (26)$$

are adsorptions of immobile component on the sides of α and β phases, respectively.

Now, let us demonstrate that the excess $\overline{\omega}$ is independent of the position of the dividing surface. For this purpose, we differentiate expression (18) with respect to z_0 at a fixed physical state. The result is reduced to the expression

$$[d\overline{\omega}/dz_0] = -\omega^\alpha + \omega^\beta, \quad (27)$$

where square brackets denote that the derivative has formal meaning and corresponds to only imaginary shift of geometric dividing surface. Substituting Eqs. (11) and (12) into formula (27), we arrive at the expression

$$[d\overline{\omega}/dz_0] = -E_k^\alpha - \left(\mu_{j(k)}^\alpha - \mu_j^\beta \right) c_j^\alpha - p^\beta, \ k = x, y. \quad (28)$$

Since the right-hand side of this expression contains only values referring to the bulk phases, we can take advantage of condition (15), which yields

$$[d\overline{\omega}/dz_0] = -E_z^\alpha - \left(\mu_{j(z)}^\alpha - \mu_j^\beta \right) c_j^\alpha - p^\beta. \quad (29)$$

Finally, using equilibrium conditions (6) and (7), we arrive at the condition

$$[d\overline{\omega}/dz_0] = -\omega^\alpha + \omega^\beta = 0. \quad (30)$$

Thus, we obtained equilibrium conditions that are analogous to those for two fluid phases, albeit using the newly introduced grand thermodynamic potential of

solids. Condition $\omega^\alpha = \omega^\beta$ can be significant in the theory of wetting [12].

Using the hybrid potential $\tilde{\Omega}$, the surface tension σ is defined as its excess per unit area of dividing surface at its particular location, when the adsorption of immobile component is equal to zero [1, 3], which corresponds precisely to the Gibbs approach. However, Gibbs also physically interpreted σ as the formation work of a new unit surface area, e.g., when cutting the body (see [4], p. 315). Let us take this interpretation as the base definition, which can be used at an arbitrary position of the dividing surface. In this case, we will follow the scheme applied in review [1] (see p. 192), but using the grand thermodynamic potential instead of the hybrid potential.

Considering the formation process of a new surface of a solid at given temperature, total volume of a system, and values of all chemical potentials μ_i^β and μ_j^β in the adjacent fluid phase, we can calculate the work of this process as the difference between the final and the initial values of the grand thermodynamic potential Ω defined by expression (8). Let the solid in the form of rectangular parallelepiped (phase α) with volume V^α be in the fluid medium (phase β) at thermodynamic equilibrium with this phase; the whole of a system is considered in a given volume. Cutting a solid into two parts (both parts remain within our system) requires the following work to be done:

$$\Delta\Omega = \left(\omega^\alpha - \omega^\beta \right) \Delta V^\alpha + \overline{\omega} \Delta A, \quad (31)$$

Here, ΔV^α is the change of the volume of solid phase (which is possible due to the choice of the dividing surface) and ΔA is the change of the surface area of the solid. Suggesting that the solid is cut by the plane parallel to one of its faces, we can see that ΔA does not depend on the position of the dividing surface at the cutting site. Using condition (30), we obtain $\Delta\Omega = \overline{\omega} \Delta A$. According to the definition of σ, this work is equal to $\sigma \Delta A$. Hence, at an arbitrary choice of solid−fluid dividing surface, we have

$$\sigma = \overline{\omega}. \quad (32)$$

Comparing this equality with expression (23), we obtain the relation (cf. relation (5.31) from [1])

$$\sigma = \gamma_k + \overline{g}_{j(k)} + \left(\mu_{j(k)}^\alpha - \mu_j^\beta \right) \Gamma_j^\alpha, \ k = x, y. \quad (33)$$

As it stems from the scalar nature of σ, the right-hand side of expression (33) is invariant with respect to the choice of direction along the surface. As can be seen from this expression, the difference in the values of mechanical and thermodynamic surface tensions originates from the presence of two terms. The term $\overline{g}_{j(k)}$ characterizes the nonuniformity of the chemical potential of the immobile component. The other term

$\left(\mu_{j(k)}^{\alpha} - \mu_j^{\beta}\right)\Gamma_j^{\alpha}$, differs from zero only at nonzero adsorption Γ_j^{α}) and, at the same time, in the presence of an anisotropy of the chemical potential of the immobile component in *the bulk* of solid. Indeed, using chemical equilibrium condition (6) for the isotropic state of solid in the bulk, we obtain $\mu_{j(x)}^{\alpha} = \mu_{j(y)}^{\alpha} = \mu_{j(z)}^{\alpha} = \mu_j^{\beta}$. This means that, in this case, the term $\left(\mu_{j(k)}^{\alpha} - \mu_j^{\beta}\right)\Gamma_j^{\alpha}$ will be equal to zero at an arbitrary choice of the dividing surface. Both properties of the chemical potential, i.e., nonuniformity and anisotropy, are typical for solids and are related to the presence of immobile components. In a fluid, chemical potentials of all components are actually scalar quantities, i.e., they are isotropic and uniform in the state of thermodynamic equilibrium in the absence of external fields. As a result, equality $\sigma = \gamma_k$. is always fulfilled in this case.

Turning back to definition (2) of σ as the specific surface excess of the grand thermodynamic potential $\overline{\omega}$, we can state that this definition can be applied not only to fluids but also to solids; moreover, this definition can be applied at an arbitrary position of the dividing surface, provided that the grand thermodynamic potential of solid is determined by expression (8). In regards to hybrid potential, the surface density of its excess expressed by formula (24) depends on the position of the dividing surface and can be identified with σ only for a particular dividing surface [1, 2]. Since it follows from expressions (23) and (24) that $\overline{\omega} = \overline{\overline{\omega}} - \mu_j^{\beta}\left(\Gamma_j^{\alpha} + \Gamma_j^{\beta}\right)$, then, taking into account equality (32) for an arbitrary dividing surface, we conclude that, at nonzero μ_j^{β} value, this particular dividing surface is necessarily equimolecular with respect to immobile component j (i.e., $\Gamma_j^{\alpha} + \Gamma_j^{\beta} = 0$). Thus, generalizing the definition of the thermodynamic surface tension σ with the aid of newly introduced grand thermodynamic potential of solids, we obtained a more convenient tool, to say nothing of the generality of this definition for fluids and solids.

Note that the mere fact of the independence of thermodynamic surface tension σ, which is originally defined as the specific work of the formation of new surface, of the position of the dividing surface is rather trivial. The formation work of a new surface cannot depend on the position of mathematical dividing surface and the area of this surface is independent of the choice of its position for the case of a planar surface (however, this will not be true for a curved surface). However, nontrivial conclusions are the independence of the surface excess $\overline{\omega}$ of the introduced grand thermodynamic potential on the position of the dividing surface, as well as universal equality (32).

CONCLUSIONS

All of the above refers to the case when the solid is at equilibrium with a real fluid. In the case when the solid is insoluble in the adjacent fluid or when this fluid is completely absent, it is possible to develop a more general approach using a hypothetical equilibrium of the solid in an arbitrary state with an imaginary fluid, the chemical potential of component j in which is equal exactly to $\mu_{j(k)}^{\alpha}$. Thus, suggesting that chemical equilibrium condition (6) is fulfilled, we can define the grand thermodynamic potential of a solid as

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_{j(z)}^{\alpha} N_j, \qquad (34)$$

in which μ_j^{β} from definition (8) is replaced by $\mu_{j(k)}^{\alpha}$. Definition (34) does not suggest the presence of the fluid phase coexisting with the solid, and the whole reported theory is formulated in general form. All of the above equalities, as well as the universal definition of the thermodynamic surface tension σ, remain valid with the substitution of μ_j^{β} for $\mu_{j(k)}^{\alpha}$. This more general approach can be used in problems where it is necessary to shift a dividing surface between a solid and a fluid, in which immobile component j of the solid is not mobile (i.e., the solid does not contact with its solution, melt, or vapor). In particular, this can be applied in the theory of wetting when studying sessile droplets [7, 8, 10, 12].

Two remarks should be made. First, the theory was formulated for uniform phases. Passing to nonuniform solids (that is very often encountered in practice), all of the equalities mentioned above should be considered to be local relations. Second, we confined ourselves to the consideration of planar surfaces. The case of curved surfaces of solids is more complicated not only because of the jump of the mechanical stress, but also because of the inequality of the chemical potential in coexisting phases. This case has yet to be studied, although the first steps in its analysis have already been made [16].

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