

Variational Method in Thermodynamics of Two-Component Charged Gas

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Abstract Based on appropriately generalized Gibbs' variational methodology, we analyzed two-component systems with electrostatic interaction. We begin by formulating isoperimetric-type variational problems, and then proceed with calculation of the first and second variations of the corresponding functionals. The first variation is used for establishing the conditions of equilibrium of the systems under study, whereas the second – is for establishing conditions of stability of equilibrium configurations. The established conditions of equilibrium permit calculating distributions of the mass densities of the components as well as distributions of entropy (or temperature) and the electric potential. To that end, we have to solve a system of four integral equations and one algebraic.

Keywords: *plasma, thermodynamics, Gibbs variational principles, plasma stability, equations of state*

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1. Introduction

J.W. Gibbs suggested two approaches in thermodynamics: statistical and variational. The latter is presented in his famous treatise "On the Equilibrium of Heterogeneous Substances" [1]. Gibbs has millions of followers, especially in what concerns his statistical method (see, for instance, [2,3]). His variational method is very popular also, especially in chemical thermodynamics (see, for instance, [4]).

We interpret the term "heterogeneous substance" in the sense of J.W. Gibbs [1]. With his millions of followers in different areas of science and engineering, it is not surprising there are hundreds of different interpretations of the Gibbs' celebrated treatise [1]. Quite often, hot debates transpire since the different interpretations are absolutely incompatible. Our own interpretation of Gibbs' principles and methodology is presented in detail in monograph [5]. In this monograph, interested readers can find discussion of different competing interpretations. Presentation in [5] mostly concerns mechanical one-component systems with substances undergoing phase transformations. At the same time, Gibbs' approach permits various generalizations. In particular, in publications [6-12] we presented how our interpretation of Gibbs' methodology can be applied to heterogeneous systems with electromagnetic interaction.

We use the terms heterogeneous for thermodynamic systems and their configurations while we deal with macroscopic physical bodies having contacts across macroscopic boundaries. The bodies can be solid, liquid or

gaseous. In paper [6] we demonstrated how our methodology can be applied to one-component charged gas.

The one-component case is simpler and results in the less cumbersome and more transparent relationships than the multicomponent case.

The necessity in the multicomponent analysis is mostly physical and absolutely straightforward: there is a humongous repulsion between the electric charges of the same sign. This repulsion can be compensated for by the fact that the humongous attraction shows up between the charges of opposite signs. This is why practically all macroscopic and nanoscale bodies (atoms and molecules) are almost electrically neutral. Therefore, for the phenomenological macroscopic analysis we have to deal with at least two-component charged liquids: the positively charged components and the negatively charged components. This is the bare minimum; quite often it is necessary to introduce many more components.

For the sake of brevity and transparency though, we will dwell on the two-component charged liquids, which will be called electronic and ionic components.

2. The System under Study

Assume that our charged liquid has two components with the mass densities $\rho^e(z)$ and $\rho^i(z)$ with the fixed total amounts of each of them:

$$\int_{\Omega} d\Omega \rho^e(z) = M^e, \quad \int_{\Omega} d\Omega \rho^i(z) = M^i, \quad (1)$$

where M^e and M^i are the total masses of the electronic and ionic liquids, and Ω is the domain, occupied by the gases. Sometimes, we place the superscripts “ e ” and “ i ” as subscripts.

Let the constants σ^e and σ^i be the charges per unit mass of the electronic and ionic liquids, respectively.

We assume that the mixture is characterized by the cooperative internal energy density U per unit volume:

$$U = U(\rho^e, \rho^i, \eta) \quad (2)$$

and the entropy density η .

We postulate the following relationship for the electrostatic energy E_{elect} :

$$E_{elect} \equiv \frac{1}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{(\sigma^e \rho^e + \sigma^i \rho^i)(\sigma^e \rho^{e*} + \sigma^i \rho^{i*})}{|\bar{z} - \bar{z}^*|} \quad (3)$$

Here and in the following, the notation ρ^{e*} means that the function ρ is treated as function of the independent spatial variable z^* , whereas the notation ρ^e is treated as function of the independent variable z .

Per the Gibbs methodology [1], when analyzing equilibrium and stability in the closed thermodynamic systems, we have to minimize the functional Φ

$$\Phi \equiv \frac{1}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{(\sigma^e \rho^e + \sigma^i \rho^i)(\sigma^e \rho^{e*} + \sigma^i \rho^{i*})}{|\bar{z} - \bar{z}^*|} + \int_{\Omega} d\Omega U(\rho^e, \rho^i, \eta) \quad (4)$$

under the mass constraints (1) and the entropy constraint

$$\int_{\Omega} d\Omega \eta(z) = S, \quad (5)$$

where S is the total entropy of the system under consideration.

In order to address this minimum problem with isoperimetric constraints (1) and (5) we have to consider the unconstrained minimum for the functional $\tilde{\Phi}$

$$\tilde{\Phi} = \int_{\Omega} d\Omega \left[U(\rho^e, \rho^i, \eta) - \Lambda^e \rho_e - \Lambda^i \rho_i - T\eta \right] + \frac{1}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{(\sigma^e \rho^e + \sigma^i \rho^i)(\sigma^e \rho^{e*} + \sigma^i \rho^{i*})}{|\bar{z} - \bar{z}^*|} \quad (6)$$

where Λ^e , Λ^i , and T are the indefinite Lagrange multipliers.

3. The First Variation and Equilibrium Conditions

Following the methodology of [5,6], we arrive at the following formula of the first variation of the functional $\tilde{\Phi}$ reads

$$\delta\tilde{\Phi} = \int_{\Omega} d\Omega \left[\begin{aligned} & \left(U_{\rho^e} - \Lambda^e + \sigma^e \int_{\Omega} d\Omega^* \frac{\sigma^e \rho^{e*} + \sigma^i \rho^{i*}}{|\bar{z} - \bar{z}^*|} \right) \delta\rho^e \\ & + \left(U_{\rho^i} - \Lambda^i + \sigma^i \int_{\Omega} d\Omega^* \frac{\sigma^e \rho^{e*} + \sigma^i \rho^{i*}}{|\bar{z} - \bar{z}^*|} \right) \delta\rho^i \\ & + (U_{\eta} - T) \delta\eta \end{aligned} \right] \quad (7)$$

Separating the independent variations in (7), we arrive at the following equations of equilibrium:

$$\begin{aligned} U_{\rho^e} + \sigma^e \int_{\Omega} d\Omega^* \frac{\sigma^e \rho^{e*} + \sigma^i \rho^{i*}}{|\bar{z} - \bar{z}^*|} &= \Lambda^e, \\ U_{\rho^i} + \sigma^i \int_{\Omega} d\Omega^* \frac{\sigma^e \rho^{e*} + \sigma^i \rho^{i*}}{|\bar{z} - \bar{z}^*|} &= \Lambda^i \end{aligned} \quad (8)$$

and

$$U_{\eta} = T \quad (9)$$

Summarizing, in order to analyze the equilibrium distributions of the charged particles and the entropy, we have to solve two integral equations (8), combined with the algebraic equation (9) and the constraints (1), (5).

4. The Second Variation and the Stability Conditions

For the second variation in vicinity of equilibrium configuration we get the following formula:

$$\delta^2\tilde{\Phi} = \int_{\Omega} d\Omega \left[\begin{aligned} & U_{\rho_e \rho_e} \delta\rho_e \delta\rho_e + 2U_{\rho_e \rho_i} \delta\rho_e \delta\rho_i \\ & + U_{\rho_i \rho_i} \delta\rho_i \delta\rho_i + 2U_{\rho_e \eta} \delta\rho_e \delta\eta \\ & + 2U_{\rho_i \eta} \delta\rho_i \delta\eta + U_{\eta\eta} \delta\eta^2 \\ & + \int_{\Omega} d\Omega^* \frac{\left(\sigma_e \sigma_e \delta\rho_e^* \delta\rho_e + 2\sigma_e \sigma_i \delta\rho_i^* \delta\rho_e \right)}{|\bar{z} - \bar{z}^*|} \end{aligned} \right] \quad (10)$$

The last relationship can be rewritten as

$$\delta^2\tilde{\Phi} = \int_{\Omega} d\Omega \left[\begin{aligned} & U_{\rho^J \rho^J} a^J a^J + 2U_{\rho^J \eta} a^J h \\ & + U_{\eta\eta} h^2 + \Sigma_{IJ} V^J a^I(z) \end{aligned} \right] \quad (11)$$

where we used the notations

$$\begin{aligned} a^I &= \delta\rho^I, h = \delta\eta, \Sigma_{IJ} = \sigma^I \sigma^J, \\ V^J(z) &= \int_{\Omega} d\Omega^* \frac{a^J(z^*)}{|\bar{z} - \bar{z}^*|} \end{aligned} \quad (12)$$

The summation indices I, J run the values e and i .

The necessary condition of stability of an equilibrium configuration is the following: the second variation $\delta^2\tilde{\Phi}$

must be non-negative for all the variations a^I and h , satisfying the (isoperimetric-type) constraints

$$\int_{\Omega} d\Omega a^I(z) = 0, \int_{\Omega} d\Omega h(z) = 0. \quad (13)$$

The last of the relationships (12) implies the Poisson equation

$$\nabla^i \nabla_i V^I = -4\pi a^I \quad (14)$$

Let us explore the extrema of the integral quadratic form (11) under the linear integral constraints (13) and the integral quadratic constraint

$$\int_{\Omega} d\Omega (a^I a^I + \kappa^2 h^2) = 1 \quad (15)$$

where κ is a positive constant.

Using again the method of indefinite multipliers we arrive at unconstrained minimization of the integral quadratic form

$$\tilde{\Pi}(a, h) \equiv \int_{\Omega} d\Omega \left[\begin{array}{l} U_{\rho^I \rho^J} a^I a^J + 2U_{\rho^I \eta} a^I h + U_{\eta\eta} h^2 \\ + \Sigma_{IJ} a^I(z) \int_{\Omega} d\Omega^* \frac{a^J(z^*)}{|\bar{z} - \bar{z}^*|} \\ - \alpha^I a^I - \beta h - \lambda (a^I a^I + \kappa^2 h^2) \end{array} \right] \quad (16)$$

where α_I , β , and λ are the Lagrange multipliers associated with the constraints (13), (15).

Varying the functional $\tilde{\Pi}$, we get the following relationship:

$$\frac{1}{2} \delta \tilde{\Pi}(a, h) \equiv \int_{\Omega} d\Omega \left[\begin{array}{l} U_{\rho^I \rho^J} a^J \delta a^I + U_{\rho^I \eta} (\delta a^I h + a^I \delta h) \\ + U_{\eta\eta} h \delta h + \delta a^I(z) \Sigma_{IJ} \int_{\Omega} d\Omega^* \frac{a^J(z^*)}{|\bar{z} - \bar{z}^*|} \\ - \frac{1}{2} \alpha^I \delta a^I - \frac{1}{2} \beta \delta h - \lambda (a^I \delta a^I + \kappa^2 h \delta h) \end{array} \right] \quad (17)$$

Separating the independent variations in (17), we arrive at the relationships

$$\left(U_{\rho^I \rho^J} - \lambda \delta_{IJ} \right) a^J + U_{\rho^I \eta} h \Sigma_{IJ} \int_{\Omega} d\Omega^* \frac{a^J(z^*)}{|\bar{z} - \bar{z}^*|} - \frac{1}{2} \alpha^I = 0 \quad (18)$$

and

$$U_{\rho^I \eta} a^I + (U_{\eta\eta} - \lambda \kappa^2) h - \frac{1}{2} \beta = 0 \quad (19)$$

In the short wavelength limit (compare with Grinfeld and Grinfeld [6,7,8]) we arrive at the algebraic spectral problem

$$\begin{bmatrix} U_{\rho_1 \rho_1} - \lambda & U_{\rho_1 \rho_2} & U_{\rho_1 \eta} \\ U_{\rho_2 \rho_1} & U_{\rho_2 \rho_2} - \lambda & U_{\rho_2 \eta} \\ U_{\rho_1 \eta} & U_{\rho_2 \eta} & U_{\eta\eta} - \kappa \lambda \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ H \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad (20)$$

Positivity of the eigenvalues of (20) is the necessary condition of stability of the equilibrium configuration.

5. Heterogeneous Systems with Two Non-deformable Solids Exchanging Free Electric Charges

Practically the same analysis can be applied to heterogeneous systems, in which two different solids have a common boundary Σ through which electric charges can freely move in both directions but are not able to change the a priori fixed position of the interface Σ neither in space nor with respect to the bodies. The only change that must be taken into account is the internal energy function $e(\rho^e, \eta)$, which now can be different for two different solids. Following changes, then required in the system 1-8: the domain Ω should be replaced with the combined domain $\Omega \rightarrow \Omega_1 \cup \Omega_2$; the equations (8), (9) should be replaced with the following ones:

$$\left(e^e \rho^e \right)_{\rho}^1 + \sigma^e \sigma^e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho^e(z^*)}{|\bar{z} - \bar{z}^*|} = \Lambda^e, \quad z^i \in \Omega_1, \quad (21)$$

$$\left(e^e \rho^e \right)_{\rho}^2 + \sigma^e \sigma^e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho^e(z^*)}{|\bar{z} - \bar{z}^*|} = \Lambda^e, \quad z^i \in \Omega_2$$

and

$$e_{\eta}^1 = e_{\eta}^2 = T, \quad z^i \in \Omega_1 \cup \Omega_2 \quad (22)$$

Further modifications required for the case for the models with electric charges concentrated on the interface or for the models with mobile interfaces. These cases will be considered elsewhere.

In the case of the spatially heterogeneous conductor the thermodynamic variables ρ and η and the thermodynamic potentials e and ψ can be different in different sub-bodies. All the above analysis remains the same, including the relationships (21) and (22). They imply, in particular:

$$\left[e_{\eta} \right]_{\pm}^+ = 0 \quad (23)$$

and

$$\left[(\rho e)_{\rho} \right]_{\pm}^+ = 0 \quad (24)$$

6. Isothermal Case

Our analysis is easy to adjust for the isothermal systems. To that end, we can forget about the entropy constraint (5) and replace the internal energy density $e(\rho, \eta)$ with the free energy density $\psi(\rho, T)$. Then, we arrive at the system

$$(\rho\psi)_\rho^1 + \sigma_e \sigma_e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho(z^*)}{|\bar{z} - \bar{z}^*|} = \Lambda, z^i \in \Omega_1, \quad (25)$$

$$(\rho\psi)_\rho^2 + \sigma_e \sigma_e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho(z^*)}{|\bar{z} - \bar{z}^*|} = \Lambda, z^i \in \Omega_2$$

The system (25) implies the relationship

$$\int_{\Omega_1 \cup \Omega_2} d\Omega \rho(\rho\psi)_\rho + \int_{\Omega_1 \cup \Omega_2} d\Omega \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\sigma^e \sigma^e \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|} = \Lambda M^e \quad (26)$$

where M^e is the total mass of the free electrons. The relationship (26) allows to eliminate the Lagrange indefinite multiplier M^e from the equations (25):

Thus, we arrive at the closed system of integral equations for the density distributions within the conductors:

$$\begin{aligned} & (\rho\psi)_\rho^1 + \sigma^e \sigma^e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho^e(z^*)}{|\bar{z} - \bar{z}^*|} \\ &= M_e^{-1} \int_{\Omega_1 \cup \Omega_2} d\Omega \rho^e (\rho^e \psi^e)_\rho \\ &+ M_e^{-1} \int_{\Omega_1 \cup \Omega_2} d\Omega \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\sigma^e \sigma^e \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|}, z^i \in \Omega_1, \\ & (\rho\psi)_\rho^2 + \sigma^e \sigma^e \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho^e(z^*)}{|\bar{z} - \bar{z}^*|} \\ &= M_e^{-1} \int_{\Omega_1 \cup \Omega_2} d\Omega \rho^e (\rho^e \psi^e)_\rho \\ &+ M_e^{-1} \int_{\Omega_1 \cup \Omega_2} d\Omega \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\sigma^e \sigma^e \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|}, z^i \in \Omega_2 \end{aligned} \quad (27)$$

For the system with one body we get a single integral equation

$$\begin{aligned} & \left(\rho^e \psi^e \right)_\rho^1 + \sigma_e \sigma_e \int_{\Omega} d\Omega^* \frac{\rho^e(z^*)}{|\bar{z} - \bar{z}^*|} \\ &= M_e^{-1} \int_{\Omega} d\Omega \rho^e \left(\rho^e \psi^e \right)_\rho \\ &+ M_e^{-1} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\sigma_e \sigma_e \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|} \end{aligned} \quad (28)$$

One can easily see that adding to ψ an arbitrary function of T , we arrive at the same equation.

7. Quasi-linear Free Energy

Consider a simple model of a quasi-linear free energy

$$\psi = \psi_0 + \gamma \rho \quad (29)$$

Then, the equation (28) reads

$$\begin{aligned} & 2\gamma\rho + \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\bar{z} - \bar{z}^*|} \\ &= 2\gamma M^{-1} \int_{\Omega} d\Omega \rho^2 + M^{-1} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|} \end{aligned} \quad (30)$$

whereas the original equation (25) reads

$$\rho + \frac{1}{2\gamma} \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\bar{z} - \bar{z}^*|} = \frac{\Lambda - \psi_0}{2\kappa} \quad (31)$$

Let $R(\bar{z} - \bar{z}^*)$ be the function such that the function

$$\rho(\bar{z}) = \frac{\Lambda - \psi_0}{2\gamma} \int_{\Omega} d\Omega^* \left(\bar{z} - \bar{z}^* \right) \quad (32)$$

appears to be the solution of (31).

Then we arrive at the following equation for Λ

$$\frac{\Lambda - \psi_0}{2\gamma} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* R(\bar{z} - \bar{z}^*) = M \quad (33)$$

allowing to rewrite the solution (32) as

$$\rho(\bar{z}) = M \frac{\int_{\Omega} d\Omega^* R(\bar{z} - \bar{z}^*)}{\int_{\Omega} d\Omega \int_{\Omega} d\Omega^* R(\bar{z} - \bar{z}^*)} \quad (34)$$

8. Two-dimensional Analogy of the Classical Model of Conductor

So far, we analyzed models with electrons distributed in the space with finite three-dimensional densities. Here, we switch to the classical models of conductors with the excess electrons distributed over conductors' surfaces only. Consider two conductors that are able to exchange electrons. As usually accepted in classical electrostatics we assume up-front that the charges distributed on the conductors' surfaces Σ_1 and Σ_2 with the two-dimensional mass densities ρ_1 and ρ_2 , and the charge densities $\tau_1 = \sigma\rho_1^e$ and $\tau_2 = \sigma\rho_2^e$ per unit area. We assume that they possess the internal energy densities per unit charge $\varepsilon_1(\rho_1, \eta_1)$ and $\varepsilon_2(\rho_2, \eta_2)$ where η_1 and η_2 . Thus, we arrive at the following isoperimetric variational problem

$$\int_{\Sigma_1 \cup \Sigma_2} d\Sigma \sigma \rho = Q, \quad (35)$$

$$\int_{\Sigma_1 \cup \Sigma_2} d\Sigma \rho \eta = H \quad (36)$$

We assume that the total energy of the system E_{tot} is comprised of the total internal energy E_{int} and total electrostatic energy given by the integrals

$$E_{tot} = E_{int} + E_{elec} = \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \rho \varepsilon(\rho, \eta) + \frac{1}{2} \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|} \quad (37)$$

where $\varepsilon(\tau_1, \eta_1)$ is the simplest model of the internal energy density.

Using the standard method of the Lagrange indefinite multipliers, we arrive at the unconditional variational problem for the functional Φ

$$\bar{\Phi} = \int_{\Sigma_1 \cup \Sigma_2} d\Sigma [\rho \varepsilon(\rho, \eta) - \lambda \rho - \theta \rho \eta] + \frac{1}{2} \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z) \rho(z^*)}{|\bar{z} - \bar{z}^*|} \quad (38)$$

where λ and θ are the indefinite Lagrange multiplier, associated with the isoperimetric constraints (35), (36), respectively.

We arrive at the following formula of the first variation $\delta \bar{\Phi}$

$$\delta \bar{\Phi} = \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \delta \rho \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z^*)}{|\bar{z} - \bar{z}^*|} + \int_{\Sigma_1 \cup \Sigma_2} d\Sigma [(\varepsilon + \rho \varepsilon_\rho - \lambda - \theta \eta) \delta \rho + \tau(\varepsilon_\eta - \theta) \delta \eta] \quad (39)$$

Thus, separating independent variations we arrive at the following conditions of equilibrium for $\bar{\xi} \in \Sigma_1 \cup \Sigma_2$:

$$\varepsilon + \rho \varepsilon_\rho - \theta \eta + \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z^*)}{|\bar{z} - \bar{z}^*|} = \lambda \quad (40)$$

$$\varepsilon_\eta = \theta \quad (41)$$

Using the relationship (41), we can rewrite (40) as

$$\varepsilon + \rho \varepsilon_\rho - \eta \varepsilon_\eta + \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z^*)}{|\bar{z} - \bar{z}^*|} = \lambda \quad (42)$$

Using (38), we arrive at the following formula of the second variation

$$\delta^2 \bar{\Phi} = \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \delta \rho(z) \delta \rho(z^*)}{|\bar{z} - \bar{z}^*|} + \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \left[(\rho \varepsilon)_{\rho\rho} (\delta \rho)^2 + 2\rho \varepsilon_{\eta\rho} \delta \eta \delta \rho + \tau \varepsilon_{\eta\eta} (\delta \eta)^2 \right] \quad (43)$$

9. One Special Case

Consider the model case when the internal energies are given by the relationships

$$\varepsilon_{1,2}(\rho, \eta) = \varepsilon_{1,2}^\circ, \quad (44)$$

where $\varepsilon_{1,2}^\circ$ are just 2 constants.

Then, the relations (39), (40) imply

$$\bar{z} \in \Sigma_1 : V_1(\xi) \equiv \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z^*)}{|\bar{z} - \bar{z}^*|} = \lambda - \varepsilon_1^\circ \quad (45)$$

$$\bar{z} \in \Sigma_2 : V_2(\xi) \equiv \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \rho(z^*)}{|\bar{z} - \bar{z}^*|} = \lambda - \varepsilon_2^\circ$$

The relationship (42) for the second variation now reads

$$\delta^2 \bar{\Phi} = \int_{\Sigma_1 \cup \Sigma_2} d\Sigma \int_{\Sigma_1 \cup \Sigma_2} d\Sigma^* \frac{\sigma^2 \delta \rho(z) \delta \rho(z^*)}{|\bar{z} - \bar{z}^*|} \quad (46)$$

According to (45), the electrostatic potential on each surface is constant, and the jump of the potentials is given by the formula:

$$V_1 - V_2 = (\varepsilon_1^\circ - \varepsilon_2^\circ) \quad (47)$$

The relationship (46) can be rewritten as

$$\delta^2 \bar{\Phi} = \frac{1}{8\pi} \int_{\Sigma_1 \cup \Sigma_2} d\Omega \nabla_i V \nabla^i V > 0 \quad (48)$$

According to (48), each equilibrium configuration is stable in the sense that the second energy variation assumes non-negative values only.

10. Conclusion

We analyzed the problems of equilibrium and stability of two-component liquid or gaseous systems with electrically charged components. Our analysis is based on the Gibbs variational approach. The Gibbs approach does not require any dynamics equations of plasma. It is also mathematically consistent since it is based on the single variational principle and does not require any further approximations. These positive features, of course, does not automatically guarantee the physical validity of the conclusions, as many researchers assume. The very

applicability of the Gibbs approach is an essential physical assumption. On the other hand, the variational Gibbs approach has a wide flexibility in the choice of the energy functionals and the thermodynamic potentials of the constituents.

We calculated explicitly the first (Eqs. 7, 39) and second variations (Eqs. 10, 43) of the relevant functionals. These formulae open the doors to further investigation of equilibrium and stability of two-component systems with electrically charged constituents.

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