Phase equilibrium pressure of dielectric system under influence of electrostatic field

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A B S T R A C T

Electrostatic field can change the pressure of dielectric system, and this effect is related to the exerted direction of the electric field. With this characteristic, enhancing mass and heat transfer can be achieved by applying external electric field. In this paper, based on the laws of thermodynamics, the fundamental equation of the dielectric system with the influences of electrostatic field was established. The mechanical equilibrium condition was deduced from this fundamental equation by the free energy criterion for thermodynamic equilibrium state, which is the effective pressure of each phases must be equal to each other. This effective pressure includes the mechanical effect of the electrostatic field on the dielectric system. It consists of two parts, real pressure within the system and the electric tension on the interface between phases, which leads to the difference of the real pressure within different phases. For a two-phase system with a planar interface, when the electric field is parallel to the phase interface, the real pressure within the phase with larger dielectric constant is larger; when the electric field is perpendicular to the phase interface, real pressure within the phase with larger dielectric constant is smaller; and while the field acts on part of the system, the real pressure in the region with electric field is higher than that without electric field. With this characteristic, the vapor pressure of gas-liquid system could be reduced with exerting electrostatic field along the direction parallel to the interface, or it could be increased when the exerting direction is perpendicular to the interface. Our conclusions derived from equilibrium thermodynamics are consistent with the electrohydrodynamic results.

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1. Introduction

Phase transitions are always accompanied by the transfers of matter and energy, such as the boiling or condensation heat transfer, the evaporation, and distillation etc. Gas-liquid phase transitions exist widely, which have important applications in the engineering of materials, energy, chemical, food, and pharmacy. Enriching and drying of food and medicines, chemical distillation separations are based on the gas-liquid phase transitions. The distillation is now the most popular method of separating mixtures in chemical industries. However, the evident disadvantage of distillation is high energy consumption, because the distillation operation requires that the mixtures should be evaporated or condensed to establish a gas-liquid two-phase system. In some cases, extreme pressure and/or temperature are required for the setting up of this system, which not only consumes much more

energy but also encounters the technology restrictions. Temperature and pressure are two basic macroscopic physical quantities involved in the phase-change processes. The traditional method of enhancing the gas-liquid phase transition is to change the system's temperature or pressure, which is closely related to the equipment investment and energy consumption, and is often limited by technologies and equipments. In addition, the quality of some substances, such as foods and medicines, is closely related to the duration of concentrating and drying, and some heat-sensitive substances have special requirements for temperatures. Therefore, developing new enhancing technology to improve the efficiency of gas-liquid phase transition and reducing the energy consumption have become a common concerned issue. Experiments indicate that the electrostatic fields can effectively affect the gas-liquid phase transition, improve the distillation efficiency [1] and enhance the heat and mass transfer [2,3].

The thermodynamic foundations of phase transitions are the phase equilibrium [4]. The equilibrium state is the final state of any isolated system, and also is the lowest energy state of the system.

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The system has uniform state parameters only when it is in thermodynamic equilibrium. A thermodynamic phase is the region which has uniform intensity quantities, and when the system consists of several phases, the equilibrium states have to satisfy certain phase equilibrium conditions. Pressure is the basic parameter to measure whether the thermodynamic system reaches the mechanical equilibrium. Saturated vapor pressure in the gas-liquid transition is one of the fundamental physical parameters of working fluid, and also is the important basic data of chemical production, scientific research and design process. Many designs of engineering processes are closely related to vapor pressure. Thus, the influences of the electrostatic fields on pressure are the key embodying of that on phase transition, and the study of this influence is of great significance to understand the transfer processes enhanced by electrostatic fields.

At present, the main methods of the studies of the influence of electrostatic fields on dielectric system are thermodynamic study [5–8], molecular simulation [9–11], electrohydrodynamic analysis [12,13], and experimental research [14–16]. The main results of the thermodynamic study and molecular simulation were that the electric field reduces the vapor pressures and increases the boiling points. The electrohydrodynamic analysis based on the dynamic behaviors of the polarized charges in the external fields. Experimental researches were mainly to measure the change in boiling point under the atmospheric pressure due to the inconvenience to measure the pressure. But all these references did not take into account the exerting directions of the electrostatic fields. In fact, the exerting directions can lead to different changes in the system's pressures. In this paper, the parameters of the electrostatic fields are introduced in the fundamental thermodynamic equations from the basic laws of thermodynamics. The thermodynamic pressure of the dielectric system with the influences of electric field is derived from the thermodynamic equilibrium criterion. The pressure varieties caused by the exerting modes of the electric field are discussed.

2. Fundamental equations of dielectric system with the influence of electrostatic fields

2.1. Two-phase system with electrostatic field parallel to interface

Except for heat transfer and volumetric work, if a thermodynamic system also exchanges energy with surroundings through other forms of work, the fundamental thermodynamic equation of this system can be generally expressed as [17–19].

$$dU = TdS - pdV + \sum \mu_i dn_i + dW \qquad (1)$$

where U represents the thermodynamic energy (internal energy) of the system, W represents other forms of work done by the outside on the system except for volumetric work. Because work is the transferred or transformed energy, W can also be regarded as the delivery of other forms of energy. For example, if there is electrostatic field acting on the system, there exists electric field energy W_e. Then, with the definition of free energy $F = U - TS$, the differential equation of free energy of a dielectric system with the influence of electric field can be expressed as

$$dF = -SdT - pdV + \sum \mu_i dn_i + dW_e \qquad (2)$$

Fig. 1 shows a two-phase dielectric system acted by electrostatic field produced by two parallel metal plates with charges Q. The area of each plate is A, and the separation of the plates is L. The electric displacement is equal to the charge density on the plate $D = Q/A$, and the relation between D and electric field intensity E is $D = \varepsilon_0 \varepsilon E$,

in which ε_0 is dielectric constant of vacuum and ε is relative dielectric constant of dielectric [12]. Both D and E are vectors, when the electric field exerted on the system along any direction, it can always be decomposed into a component $E_t (D_t)$ which is parallel to the interface and a component $E_n (D_n)$ which is perpendicular to the interface, or the electric field acts only on a part of the system. Therefore, without the loss of generality, the exerting manners of the electric field on a two-phase system can be divided into the three ways, which is show in Fig. 1.

The electrostatic energy of dielectric system is [12] $W_e = V(D^2/2\varepsilon_0\varepsilon)$. As for the first case shown in Fig. 1 (a), the change in volume is displayed by the change in the area of the plates when the phase transfer occurs. Consequently, the amount of electric charges in each phase also changes, so the electric field energy in each phase can be rearranged as $W_e = (L^2/2\varepsilon_0)(Q^2/\varepsilon V)$. Dielectric constant is not sensitive to an ordinary electric field, therefore, it is only the function of temperature and density, that is

$$d\varepsilon = \sum \frac{\varepsilon_\rho}{V} M_i dn_i - \frac{\rho}{V}\varepsilon_\rho dV + \varepsilon_T dT \qquad (3)$$

The density is $\rho = \sum M_i n_i / V$, and define $\varepsilon_\rho \equiv (\partial \varepsilon / \partial \rho)_T$, $\varepsilon_T \equiv (\partial \varepsilon / \partial T)_\rho$. Then with Eq. (3), the differential expression of the electric field energy can be expressed as

$$dW_e = -\frac{L^2 Q^2 \varepsilon_T}{2\varepsilon_0 \varepsilon^2 V} dT + \frac{L^2 Q^2}{2\varepsilon_0 \varepsilon^2 V^2}(\rho\varepsilon_\rho - \varepsilon)dV + \frac{L^2 Q}{\varepsilon_0 \varepsilon V} dQ$$
$$- \sum \frac{L^2 Q^2 \varepsilon_\rho}{2\varepsilon_0 \varepsilon^2 V^2} M_i dn_i \qquad (4)$$

Substituting Eq. (4) into Eq. (2) leads to the differential free energy of the dielectric system with the influence of electrostatic field

$$dF = -\left(S + \frac{L^2 Q^2 \varepsilon_T}{2\varepsilon_0 \varepsilon^2 V}\right)dT - \left[p - \frac{L^2 Q^2 (\rho\varepsilon_\rho - \varepsilon)}{2\varepsilon_0 \varepsilon^2 V^2}\right]dV$$
$$+ \sum \left(\mu_i - \frac{L^2 Q^2 \varepsilon_\rho}{2\varepsilon_0 \varepsilon^2 V^2} M_i\right)dn_i + \frac{L^2 Q}{\varepsilon_0 \varepsilon V} dQ \qquad (5)$$

For the sake of simplifying the expression, give the definitions of $S' \equiv S + \frac{L^2 Q^2 \varepsilon_T}{2\varepsilon_0 \varepsilon^2 V}$, $p' \equiv p - \frac{L^2 Q^2 (\rho\varepsilon_\rho - \varepsilon)}{2\varepsilon_0 \varepsilon^2 V^2}$, $\mu_i' \equiv \mu_i - \frac{L^2 Q^2 \varepsilon_\rho}{2\varepsilon_0 \varepsilon^2 V^2} M_i$, $\zeta \equiv \frac{L^2 Q}{\varepsilon_0 \varepsilon V}$, then Eq. (5) can be simplified as

$$dF = -S'dT - p'dV + \sum \mu_i' dn_i + \zeta dQ \qquad (6)$$

On the right side of this equation, the temperature T, the volume V, the amount of substance n and the free charge Q are independent variables. Thus, the thermodynamic behavior of the dielectric system can be completely determined by Eq. (6) [20].

2.2. Two-phase system with electrostatic field perpendicular to the interface

For the second case shown in Fig. 1(b), when the electrode plates are arranged parallel to the two-phase interface, the electric field is perpendicular to the interface. In this case, both the area of the electrode plates and the free charges on them remain constant during the phase transition, hence the electric displacement also remain unchanged. Thus, the electric field energy can be rearranged as $W_e = (D^2/2\varepsilon_0)(V/\varepsilon)$. With the differential Eq. (3), the differential of electric field energy of this dielectric system can be obtained