Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Complex pole approach in thermodynamic description of fluid mixtures with small number of molecules

Timur Aslyamov [a],*, Oleg Dinariev [b]

[a] *Moscow Institute of Physics and Technology, Russia*
[b] *Schlumberger Moscow Research Center, Russia*

ABSTRACT

The subject matter of classical thermodynamics is the asymptotic behavior of equilibrium systems in thermodynamic limit, for small molecular systems, when transition to thermodynamic limit is impossible, the extension of thermodynamics is required. This work studies novel approach for the evaluation of partition functions of small systems by complex pole analysis. Several cases for molecular systems in small cavities are studied numerically. In particular size-dependent additional pressure for small systems is evaluated analytically and numerically. Similar approach was developed earlier in nuclear physics for finite systems of nucleons. The obtained results correspond to published experimental data and molecular dynamics simulations.

1. Introduction

The subject matter of classical thermodynamics is the asymptotic behavior of equilibrium systems under the assumption, that the volume V and the number of particles are large, while the ratio of these quantities is finite. The transition to this asymptotic behavior is called thermodynamic limit. However, there are many systems, which by their physical nature do not permit thermodynamic limit. For instance, a gas mixture in a small cavity inside solid can behave quite differently depending on the size of the cavity. The necessity to extend thermodynamics in order to describe non-classical behavior of small equilibrium systems was understood long ago [1,2]. The non-classical thermodynamic effects were identified and studied in different areas of science, like chemical physics, biology, and nuclear physics [3–5]. Small systems can deviate from classical thermodynamics in adsorption and droplet formation [6–8], anomalous fluctuations [9,10], breakdown of equivalence of statistical ensembles [11–13], and loss of additive property of thermodynamic potentials [14]. These examples demonstrate various phenomena, which require extension of thermodynamics beyond thermodynamic limit.

The scientific motivation of the present research is the need to improve theoretical understanding of artificial and natural materials with nanopores, which is expected to lead to quantitative description of such systems. Accordingly a wide range of potential applications can be envisaged: from better evaluation of volatile components in porous solids to the better control of solid quality. In the present work we study several specific features of gas–liquid mixtures with small number of molecules occupying finite volume. The analysis is performed in the frame of equilibrium statistical physics using ideas developed earlier for finite system of nucleons [15]. Also this work is motivated by an outstanding paper [16], where extension of standard mean-field theory is developed for mesoscopic systems. The authors use the assumption that each molecule with multiple degrees of freedom can be represented as a lattice gas particle with known mean-field solution. In the present framework, statistic of single cluster formation is based on Fisher droplet model [17]. It is a well known method that contains information about volume and surface energy. Implementing Fisher assumptions for separate clusters we develop statistical theory for real mixtures with account of small-size effects. Our results agree with previously published experimental and theoretical results, in particular, we derive the expression for additional pressure, which exhibits oscillations in respect to the pore width [18]. It should be noted, that the study of partition sum in the complex plane was proposed in [19], as a tool to extend the definition of phase transitions to small systems. These techniques were successfully applied to different physical systems [20,21].

Using capillarity assumption only for single cluster we can get statistical theory for real system which takes into account properties of small systems.

---

* Corresponding author.
  E-mail address: t.aslyamov@gmail.com (T. Aslyamov).

2. Results and discussion

We consider gas–liquid mixture, which contains M chemical components, in metastable zone using Fisher droplet model [17]. It is assumed, that the mixture is inside small cavity with non-wetting walls. We use physical units with normalization in respect to Planck and Boltzmann constants $\hbar = k_B = 1$. Also we use notations: $\boldsymbol{m} = (m_i)$, is a set of molecular masses of component with number i, $i = 1, ..., M$; $\boldsymbol{N} = (N_i)$ is a set of numbers representing actual amounts of different molecules; $\boldsymbol{b} = (b_i)$ is a set of volumes of molecules, which are assumed close to spherical; $\boldsymbol{\mu} = (\mu_i)$ is a set of chemical potentials; V, T are volume and temperature respectively. Small droplet (cluster) is characterized by set of integers $\boldsymbol{k} = (k_i)$, which are numbers of molecules of different types belonging to the cluster. The number of clusters with fixed vector $\boldsymbol{k}$ is denoted $n_{\boldsymbol{k}}$, the energies per molecule in the cluster are denoted by $\boldsymbol{w} = (w_i)$. We use scalar products:

$$(\boldsymbol{k}, \boldsymbol{m}) = \sum_{i=1}^{M} k_i m_i, \qquad (\boldsymbol{k}, \boldsymbol{b}) = \sum_{i=1}^{M} k_i b_i,$$

$$(\boldsymbol{k}, \boldsymbol{\mu}) = \sum_{i=1}^{M} k_i \mu_i, \qquad (\boldsymbol{k}, \boldsymbol{w}) = \sum_{i=1}^{M} k_i w_i.$$

The one-component case $M = 1$ was recently considered in [22].

Under the assumptions of Fisher droplet model the partition function for a single cluster can be calculated as following

$$q_{\boldsymbol{k}} = V f_{\boldsymbol{k}} = V \left(\frac{m_{\boldsymbol{k}} T}{2\pi} \right)^{3/2} e^{-\frac{\phi_{\boldsymbol{k}}}{T}}. \qquad (1)$$

Here $m_{\boldsymbol{k}} = (\boldsymbol{k}, \boldsymbol{m})$ is droplet mass, $\phi_{\boldsymbol{k}} = (36\pi)^{1/3}\sigma \times (\boldsymbol{k}, \boldsymbol{b})^{2/3} - (\boldsymbol{k}, \boldsymbol{w})$ is droplet potential energy, σ is surface energy. If the mixture is described as an ideal gas of clusters, then in the frame of canonical ensemble (CE) the partition function can be calculated as following

$$Q(V, T, \boldsymbol{N}) = \prod_{\boldsymbol{k}} \sum_{n_{\boldsymbol{k}}} \frac{q_{\boldsymbol{k}}^{n_{\boldsymbol{k}}}}{n_{\boldsymbol{k}}!} \delta \left(\boldsymbol{N} - \sum_{\boldsymbol{k}} \boldsymbol{k} n_{\boldsymbol{k}} \right) \qquad (2)$$

with Dirac delta-function providing molecular balance condition $\boldsymbol{N} = \sum_{\boldsymbol{k}} \boldsymbol{k} n_{\boldsymbol{k}}$.

Evident limitations of the model (1), (2) arising from the ideal gas approximation can be remediated by the following corrections. First, one can take account of non-zero volume of clusters by the following substitution in Eq. (1):

$$V \to V_{\text{eff}} = V - \sum_{\boldsymbol{k}} (\boldsymbol{k}, \boldsymbol{b}) n_{\boldsymbol{k}}. \qquad (3)$$

Second, one can introduce geometrical restrictions on the size of the cluster by additional condition $(\boldsymbol{k}, \boldsymbol{b}) \leq K(V)$ in the partition function expression (2). Here the volume-dependent function $K(V)$ implicitly characterizes the actual geometry of the cavity or pore with volume V. It is possible, that $K(V)$ is constant, if there is size restriction in certain direction, for example, for the parallelepiped cavity with one size being fixed and two others being arbitrary.

After these modifications the CE partition function has the following form

$$Q(V, T, \boldsymbol{N}) = \prod_{\boldsymbol{k}}^{(\boldsymbol{k}, \boldsymbol{b}) \leq K(V)} \sum_{n_{\boldsymbol{k}}} \frac{(f_{\boldsymbol{k}} V_{\text{eff}})^{n_{\boldsymbol{k}}}}{n_{\boldsymbol{k}}!}$$
$$\times \delta \left(\boldsymbol{N} - \sum_{\boldsymbol{k}} \boldsymbol{k} n_{\boldsymbol{k}} \right) \Theta(V_{\text{eff}}) \qquad (4)$$

with Heaviside function Θ providing geometrical restriction on the number of clusters $\sum_{\boldsymbol{k}} (\boldsymbol{k}, \boldsymbol{b}) n_{\boldsymbol{k}} \leq V$. The direct calculation of the partition function is complicated because of the overlapping constraints on the cluster size, number of clusters and number of molecules. The way to overcome this difficulty was developed in nuclear physics [15], where similar problems are encountered for the finite systems of nucleons. The first step is the transition from CE to grand canonical ensemble (GCE), which removes restriction on the number of molecules. Let us point out that our approach with GCE is based on the assumption, that while we consider a finite-size void, we still assume the mixture to be an open system. For example, there can be molecular exchange with external reservoir via molecular-size defects in the walls. The CE approach for closed system could lead to different results. The example of such discrepancy between CE and GCE was demonstrated in [23].

The CE partition function is replaced by the following GCE partition function

$$\Xi(V, T, \boldsymbol{\mu}) = \sum_{\boldsymbol{N}} Q(V, T, \boldsymbol{N}) \exp \frac{(\boldsymbol{\mu}, \boldsymbol{N})}{T}$$
$$= \prod_{\boldsymbol{k}}^{(\boldsymbol{k}, \boldsymbol{b}) \leq K(V)} \sum_{n_{\boldsymbol{k}} = 0}^{\infty} \frac{[f_{\boldsymbol{k}} V_{\text{eff}} \exp \frac{(\boldsymbol{k}, \boldsymbol{\mu})}{T}]^{n_{\boldsymbol{k}}}}{n_{\boldsymbol{k}}!} \Theta(V_{\text{eff}}) \qquad (5)$$

The second step is the Laplace transform of the GCE partition function in respect to the volume V, which helps to deal with interconnected volume and cluster restrictions

$$\hat{\Xi}(\lambda, T, \boldsymbol{\mu}) = \int_{0}^{\infty} dV e^{-\lambda V} \Xi(V, T, \boldsymbol{\mu}) \qquad (6)$$

Once the Laplace transform (6) is known, it is possible to reconstruct the partition function (5) by inverse Laplace transform

$$\Xi(V, T, \boldsymbol{\mu}) = \frac{1}{2\pi i} \int_{\chi - i\infty}^{\chi + i\infty} d\lambda e^{\lambda V} \hat{\Xi}(V, T, \boldsymbol{\mu}) \qquad (7)$$

Here the integration path must be chosen to lie at the right side of integrand singularities λ_n, $n = 0, 1, 2, \ldots$, which are simple poles usually. These poles satisfy the equation

$$\lambda = \Phi(\lambda, V, T, \boldsymbol{\mu}) = \sum_{\boldsymbol{k}}^{(\boldsymbol{k}, \boldsymbol{b})} f_{\boldsymbol{k}} \exp \frac{(\boldsymbol{k}, \boldsymbol{\mu}) - (\boldsymbol{k}, \boldsymbol{b}) T \lambda}{T} \qquad (8)$$

Calculating the sum of residues over the poles in (7) we arrive at the following result

$$\Xi(V, T, \boldsymbol{\mu}) = \sum_{\lambda_n} e^{\lambda_n V} \left(1 - \frac{\partial \Phi(\lambda_n)}{\partial \lambda} \right)^{-1} \qquad (9)$$

While the expression (9) for the GCE partition function is derived analytically, the actual computation of the poles λ_n and the sum (9) is done numerically with specific values of the governing parameters. The practical usefulness of this approach comes from the fact that in some cases the summation over small number of poles in (9) is sufficient to provide effective approximation for the partition function with clear physical interpretation. Let us consider this issue in more detail.

Let us introduce real R_n and imaginary I_n parts of the poles $\lambda_n = R_n + i I_n$. We enumerate poles in a such way, that $n = 0$ corresponds to the only real solution $\lambda_0 = R_0$ with a largest real part value $R_0 > R_{n > 0}$. All other poles possess non-zero imaginary parts and complex conjugate doubles. In accordance with (9) the poles are parametrically dependent on V, T, $\boldsymbol{\mu}$. Typical distribution of