



Pitfalls of using the geometric-mean combining rule in the density gradient theory



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ABSTRACT

It is popular and attractive to model the interfacial tension using the density gradient theory with the geometric-mean combining rule, in which the same equation of state is used for the interface and bulk phases. The computational efficiency is the most important advantage of this theory. In this work, it has been mathematically shown that the theory fails if the solution profile is not monotonic in the path function, which is defined as the summation of the density multiplied by the square root of the influence parameter over all components. A computational solution procedure is then presented by specifying the path function, in which a reference component is not needed. The differences of the chemical potential between the interface and the bulk phases, and the tangent plane distance have been used to analyze the characteristics of the solution profile from the geometric-mean density gradient theory. It has been found that the solution profile passes a saddle point of the tangent plane distance, which is independent of the influence parameters. It has been shown that the numerical pitfalls could occur for both vapor–liquid and liquid–liquid equilibrium systems. Shape density change inside the interface could be considered as a warning for the unsuccessful applications of the geometric-mean density gradient theory combined with the chosen thermodynamic model, even if numerical pitfalls do not occur.

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1. Introduction

It is attractive to model the interfacial tension with the density gradient theory (DGT) combining the same equation of state (EOS) used for phase equilibrium calculations, because it is a theoretically sound, consistent and computationally affordable approach [1–13]. According to the work of Wu [14], the DGT and the density functional theory (DFT) have the same mathematical fundamental – calculus of variations. The computation of the DGT is more efficient, because the DGT assumes that the total Helmholtz energy of an inhomogeneous fluid, e.g. an interface, consists of the Helmholtz energy of a homogeneous fluid with the same local densities and another contribution from the local density gradients, which are independent on the local densities, adjusted by the so-called influence parameters.

It is quite common to use the geometric-mean combining rules for the influence parameters [1–6], which dramatically

reduce the computational cost and also makes the theory predictable. There are different numerical approaches for implementing the geometric-mean DGT to calculate the interfacial tension. One is choosing the density of one of the components as an independent variable to define the density profiles. The density of the chosen component has to be monotonic, not necessarily in the entire interfacial region, in which case independent variables have to be switched when it reaches a minimum or maximum point. Another approach is introducing a new independent variable to define the density path profiles, which then is called as a path function. Cornelisse proposed three empirical path functions for binary mixtures and used one of them, in which two iteration loops are needed to adjust the path function in an outer loop [2].

The geometric-mean DGT gains significant computational efficiency because of using a limiting value in the combining rule. Therefore, people might suspect that the approach implies a risk of failures. In this work, the third path function proposed by Cornelisse [2] is generalized within a rigorous mathematical framework to study the characteristics of the solution profile from the geometric-mean DGT for both unproblematic and problematic

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cases, based on the observation that the path function has to be monotonic along the solution profile.

The rest of this work is organized as follows: the methodology, e.g. density gradient theory, the path function, the solution procedure and the characteristics of the solution profile, etc., is presented in Section 2; the detailed results of unproblematic and problematic applications of the geometric-mean DGT are discussed in Section 3, followed by the conclusions in Section 4.

2. Theory

When the DGT is applied to the interfacial behavior calculations, the Helmholtz free energy of the interface can be expressed as:

$$F = A \int_{-\infty}^{\infty} \left[f_0 + \frac{1}{2} \sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right] dz \quad (1)$$

Where F is the total Helmholtz free energy; f_0 is the Helmholtz free energy density of the homogeneous fluid with the density at the local point; c_{ij} is the influence parameters between molecules i and j ; $\{d\rho_i/dz\}$ is the density gradient along the interfacial spatial dimension z ; A is the interfacial area. The equation can be understood that the total Helmholtz free energy consists of two contributions: a reference one, which is a function of local density and counted by the same equation of state model used for the bulk phases and a correction one, or the gradient term, which is a function of the local density gradients. Therefore the DGT is also called as square/squared-gradient theory, or simply gradient theory.

At equilibrium, the total Helmholtz free energy of the interface has to be minimized with the constraint of constant molecular numbers. If the influence parameters are assumed density independent, the following Euler–Lagrange equations can be reached:

$$\sum_j c_{ij} \frac{d^2 \rho_j}{dz^2} = \mu_i - \mu_{i,b} \quad (2)$$

Where μ_i and $\mu_{i,b}$ are the chemical potentials of component i at the local point in the interface and in the bulk phases, respectively. This set of equations defines the interfacial density profiles.

By definition, the interfacial tension can be calculated by the following equation [2]:

$$\begin{aligned} \sigma &= \int_{-\infty}^{\infty} \left(f_0 + \frac{1}{2} \sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} - \sum_i \rho_i \mu_{i,b} + P_b \right) dz \\ &= \int_{-\infty}^{\infty} \left[\frac{1}{2} \sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} + \sum_i \rho_i (\mu_i - \mu_{i,b}) - (P - P_b) \right] dz \end{aligned} \quad (3)$$

If Equation (2) is multiplied by dn_i/dz , summed over index i and integrated over z , the following relation can be reached:

$$\frac{1}{2} \sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} = \sum_i \rho_i (\mu_i - \mu_{i,b}) - (P - P_b) = tpd \quad (4)$$

Where P and P_b are internal pressure at local density and the equilibrium pressure of bulk phases, respectively. The right hand side (RHS) is actually the tangent plane distance (tpd) for the bulk phases, so for stable bulk phases the RHS is always non-negative.

Substituting Equation (4) into Equation (3), the interfacial tension can then be calculated as:

$$\begin{aligned} \sigma &= \int_{-\infty}^{\infty} \left(\sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right) dz \\ &= \int_{-\infty}^{\infty} 2 \left[\sum_i \rho_i (\mu_i - \mu_{i,b}) - (P - P_b) \right] dz \end{aligned} \quad (5)$$

The detailed derivation can be found in the literature [2].

In general, the influence parameters c_{ij} between molecules i and j can be obtained from those of pure fluids by a similar combining rule used in the EOS pure component parameters:

$$c_{ij} = (1 - \beta_{ij}) \sqrt{c_i c_j} \quad (6)$$

As discussed by Cornelisse [2], β_{ij} cannot be chosen arbitrarily. A negative value or a value larger than 2 would permit a negative contribution of unlimited magnitude from the gradient term and the minimization would result in a surface tension of negative infinity.

It is widely used to set β_{ij} zero, i.e. the geometric-mean combining rule. The geometric-mean DGT will be the only case discussed in this work. This drastically simplifies the solution procedure, and in addition, makes the approach predictive, since no new adjustable parameters are required for binaries. As zero is one limiting value of β_{ij} , however, one might suspect that the approach implies a risk of failures.

2.1. A path function

With the geometric-mean combining rule, we obtain,

$$\sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} = \left(\sum_j \sqrt{c_j} \frac{d\rho_j}{dz} \right)^2 = \left(\frac{ds}{dz} \right)^2 \quad (7)$$

Where

$$s = \sum_j \sqrt{c_j} \rho_j \quad (8)$$

With Equation (8), the Equation (2) can then be rearranged:

$$\sum_j c_{ij} \frac{d^2 \rho_j}{dz^2} = \sqrt{c_i} \sum_j \sqrt{c_j} \frac{d^2 \rho_j}{dz^2} = \mu_i - \mu_{i,b} \quad (9)$$

$$\frac{\mu_i - \mu_{i,b}}{\sqrt{c_i}} = \sum_j \sqrt{c_j} \frac{d^2 \rho_j}{dz^2} = \frac{d^2 s}{dz^2} = \alpha \quad (10)$$

This set of Equation (10) related the set of $NC+1$ unknown variables $\{\rho_i, i=1,2,\dots,NC\}$ and α , and it defines a parametric curve. A tracing procedure, e.g. that proposed by Larsen et al. [13], can be used to generate the density profile connecting the two bulk phases. NC is the number of components in the system. Once the density profile is calculated, we may proceed to calculate the interfacial tension. However, the interfacial tension or the density profile can be calculated by using s as the control variable, as presented below.

By substituting Equation (7) into Equation (5), we obtain:

$$\sigma = \int_{-\infty}^{\infty} \left(\sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right) dz = \int_{-\infty}^{\infty} \left(\frac{ds}{dz} \right)^2 dz = \int_{s^V}^{s^L} \frac{ds}{dz} ds \quad (11)$$

Where s^V and s^L are calculated from Equation (8) with the densities

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