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On the Variational Properties of Scott and van der Waals "One-Fluid" Theories of Mixtures

G. Ali Mansoori

Department of Energy Engineering, University of Illinois at Chicago Circle, Chicago, Illinois 60680

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In light of the Gibbs–Bogoliubov inequality for the Helmholtz free energy of the classical systems, the variational properties of Scott and van der Waals "one-fluid" theories of mixtures with Lennard-Jones potential functions are studied. It is shown that, while the Scott's theory gives an upper bound for the Helmholtz free energy of mixtures, it is not certain whether this upper bound is a least upper bound. It is also shown that the van der Waals theory is an approximation in order to get the upper bound on the entropy of mixtures.

Let us consider two different thermodynamic systems with N particles in each system and with the same temperature. Let us also call one of these systems, the trial system, and the other one the true system. It has been shown that the following inequality holds for the difference between the Helmholtz free energies of these two systems[1,2]:

$$A \leq A_0 + \langle U - U_0 \rangle_0. \tag{1}$$

The angle brackets mean the expectation over the trial system. This inequality is in accordance with Gibbs–Bogoliubov inequality.[3] Similarly one can write

$$A - \langle U \rangle \geq A_0 - \langle U_0 \rangle. \tag{2}$$

The angle brackets in the second inequality mean the expectation over the true system. By considering the definition of entropy,

$$TS = \langle U \rangle - A,$$

from inequality (2) we get

$$TS \leq \langle U_0 \rangle - A_0. \tag{3}$$

The right-hand sides of the inequalities (1) and (3) are actually the upper bounds of the A and TS of the true system, respectively, and for simplicity we call them "ubA" and "ubS,"

$$ubA = A_0 + \langle U - U_0 \rangle_0, \tag{4}$$

$$ubS = \langle U_0 \rangle - A_0. \tag{5}$$

In the case where the true system consists of a mixture and the trial system consists of a pure component, both with Lennard-Jones intermolecular potential functions, we will have

$$U = \tfrac{1}{2} \sum_{\alpha,\beta} \sum_{i\neq j} 4\epsilon_{\alpha,\beta}[(\sigma_{\alpha,\beta}/r_{ij})^{12} - (\sigma_{\alpha,\beta}/r_{ij})^{6}], \tag{6}$$

$$U_0 = \tfrac{1}{2} \sum_{i\neq j} 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}]. \tag{7}$$

Considering (6) and (7), in order to find the least upper bound for A, it is necessary to find the values of ϵ and σ of the trial system which satisfy the following relations:

$$\partial(ubA)/\partial\epsilon = 0 \quad \text{and} \quad \partial(ubA)/\partial\sigma = 0. \tag{8}$$

This will lead us to the following relations for ϵ and σ of the pure trial system[4]:

$$\epsilon\sigma^{6} = \sum_{\alpha,\beta} x_\alpha x_\beta \epsilon_{\alpha,\beta} \sigma_{\alpha,\beta}{}^{6}, \tag{9a}$$

$$\epsilon\sigma^{12} = \sum_{\alpha,\beta} x_\alpha x_\beta \epsilon_{\alpha,\beta} \sigma_{\alpha,\beta}{}^{12}. \tag{9b}$$

Similarly, for finding the least upper bound for TS, we must have

$$\partial(ubS)/\partial\epsilon = 0 \quad \text{and} \quad \partial(ubS)/\partial\sigma = 0 \tag{10}$$

and this will lead us to the following relations between the trial system and the true system:

$$B_{12} = C_{12} \tag{11a}$$

and

$$B_6 = C_6, \tag{11b}$$

where $B_n = \langle r^{-n} \rangle_0$ and $C_n = \langle r^{-n} \rangle$. Relations (9a), (9b) and (11a), (11b) only satisfy the necessary conditions (8) and (9) for minimum ubA and minimum ubS, respectively. In order to have also sufficient conditions, relations (9a), (9b) and (11a), (11b) should also satisfy Relations (12) and (13), as given below, respectively,

$$\partial^2(ubA)/\partial\epsilon^2 > 0, \tag{12a}$$

$$\partial^2(ubA)/\partial\sigma^2 > 0, \tag{12b}$$

$$[\partial^2(ubA)/\partial\epsilon^2][\partial^2(ubA)/\partial\sigma^2] - [\partial^2(ubA)/\partial\epsilon\partial\sigma]^2 < 0, \tag{12c}$$

and

$$\partial^2(ubS)/\partial\epsilon^2 > 0, \tag{13a}$$

$$\partial^2(ubS)/\partial\sigma^2 > 0, \tag{13b}$$

$$[\partial^2(ubS)/\partial\epsilon^2][\partial^2(ubS)/\partial\sigma^2] - [\partial^2(ubS)/\partial\epsilon\partial\sigma]^2 < 0. \tag{13c}$$

After a straightforward, but tedious, calculation, the conditions (12a), (12b), (13a), and (13b) all will end up with the following conditions:

$$B_{24} - B_{12}^2 > 0, \tag{14a}$$

$$B_{12} - B_6^2 > 0. \tag{14b}$$

Also conditions (12c) and (13c) both will end up with the following unique condition:

$$-(B_{24} - B_{12}^2)(B_{12} - B_6^2) + B_{18}(B_{18} - 2B_{12}B_6) < 0. \tag{14c}$$

Conditions (14a) and (14b) hold, since the left-hand sides of these inequalities are always positive. For condition (14c), one can not prove either way whether it holds or not. Consequently, it is not generally true that relations (9a), (9b) and (11a), (11b) will minimize ubA and ubS, respectively.

Equations (9a), and (9b) are in accordance with the "one-fluid" theory of Scott for mixtures.[5,6] Insertion of (9a) and (9b) in the right-hand side of the inequality (1) will give[4]

$$A \leq A_0. \tag{15}$$

Inequality (15) clearly indicates that the "one-fluid" theory of Scott gives an upper bound for the Helmholtz free energy of mixture, but this upper bound is not necessarily the least upper bound, and it is up to the condition (14c) to be satisfied in order to get the least upper bound for A.

Equations (11a) and (11b) when replaced in the right-hand side of the inequality (3) give the following inequality:

$$TS \leq \langle U_0\rangle_0 - A_0 \tag{16}$$

or

$$S \leq S_0. \tag{17}$$

Inequality (17) indicates that if one can solve Eqs. (11a) and (11b) for a unique set of ϵ and σ of the pure trial system with respect to $\epsilon_{\alpha,\beta}$, $\sigma_{\alpha,\beta}$ of the true mixture system, one would get a mixing rule through which the upper bound for the entropy of mixture could be calculated. Equations (11a) and (11b) generally can not be solved analytically for ϵ and σ, but an approximation to these equations will give the following relations[7]:

$$\sigma^3 = \sum_{\alpha,\beta} x_\alpha x_\beta \sigma_{\alpha,\beta}^3, \tag{18a}$$

$$\epsilon\sigma^3 = \sum_{\alpha,\beta} x_\alpha x_\beta \epsilon_{\alpha,\beta}\sigma_{\alpha,\beta}^3. \tag{18b}$$

Equations (18a) and (18b) will satisfy (11a) and (11b) in the case when the terms of order $(1/KT)^2$ are negligible. Equations (18a) and (18b) are in accordance with van der Waals theory of mixtures.[8] It has been shown that the system of Eqs. (18a) and (18b) is a better mixing rule than (9a) and (9b) for predicting the thermodynamic properties of mixtures.[8]

In the case where the trial system consists of a pure soft sphere and the true system consists of a mixture of soft spheres, the Helmholtz free energy, A, and entropy, S, of the true mixture system will both have least upper bounds.

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