THE SELF-CONSISTENCY CORRECTION TO HOMOGENEOUS NUCLEATION: EXTENSION TO BINARY SYSTEMS

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Abstract—The recently presented self-consistency correction to homogeneous nucleation theory is extended to binary homogeneous nucleation. A new expression for the nucleation rate is derived. The significance of the new expression is considered in water–ethanol and water–sulphuric acid systems using three different models based on binary classical nucleation theory: the standard one, the original one and the explicit cluster model. The self-consistent correction factor will increase nucleation rates by some orders of magnitude.

Recently Girshick and Chiu (1990) have given an expression for the homogeneous homomolecular nucleation rate based on the kinetic nucleation theory developed by Katz and Wiedersich (1977). The same self-consistency correction (scc) to homogeneous nucleation was later derived by Girshick (1991) within the context of the classical nucleation theory by considering the self-consistency of the Gibbs free energy of cluster formation. The scope of this paper is to extend the correction to binary systems and to derive an expression for the nucleation rate.

The Gibbs free energy of formation of a liquid cluster in a binary mixture of vapours is given by the expression (e.g. Yue and Hamill, 1979):

\[ \Delta G = n_i (\mu_{li} - \mu_{lg}) + n_b (\mu_{lb} - \mu_{bg}) + 4\pi r^2 \sigma, \]

where \( n_i \) is the number of molecules of species \( i \), \( \mu_{li} \) and \( \mu_{lg} \) are chemical potentials of species \( i \) in the liquid and gas phase, respectively, \( r \) is the radius of the cluster and \( \sigma \) is the surface tension. \( r \) is given by

\[ \frac{4}{3} \pi r^3 = n_a v_a + n_b v_b, \]

where \( v_a \) is the volume of molecule \( a \) and \( v_b \) is the volume of molecule \( b \).

The inconsistency of the classical theory arises from the fact that for a monomer the \( \Delta G \) given by equation (1) is not equal to zero. In the homomolecular case the equation for \( \Delta G \) is made self-consistent by subtracting free energy change of a monomer. (Note that the self-consistency could be assured by using any function that makes the \( \Delta G \) of a monomer vanish (Ford, 1991). Here we want to present a simple extension of the scc-model of Girshick and Chiu.) Now, in binary nucleation, we have two kinds of monomers, which makes the situation a bit complicated compared to the one-component system. Consider a cluster consisting of \( n_a + n_b \) molecules: which is the one whose free energy change should be subtracted in order to make the \( \Delta G \) for the cluster self-consistent? A straightforward way to deal with the problem is to reduce it to the homomolecular case by imagining that the cluster \( (n_a, n_b) \) consists of \( n_a + n_b \) “virtual monomers” composed of \((1 - X)\) parts of molecule \( a \) and \( X \) parts of molecule \( b \). Here \( X \) is

\[ X = \frac{n_b}{n_a + n_b}, \]

and the molecular volume of this virtual monomer is

\[ v = (1 - X) v_a + X v_b. \]
The change in the chemical potential during the transformation from the gas phase to the liquid phase for each component is given by the following relationship

$$\mu_i - \mu_{i,sol} = -kT \ln \frac{p_i}{p_{i,sol}}$$

(5)

where $p_{i,sol}$ is the partial vapour pressure of species $i$ over a flat surface of the solution. The following quantities can be defined

- $A_{ag} = p_a/p_{as}$ = activity of component $a$ in the gas phase
- $A_{bg} = p_b/p_{bs}$ = activity of component $b$ in the gas phase
- $A_{al} = p_{a,sol}/p_{as}$ = activity of component $a$ in the liquid phase
- $A_{bl} = p_{b,sol}/p_{bs}$ = activity of component $b$ in the liquid phase,

where $p_{as}$ and $p_{bs}$ are the respective equilibrium vapour pressures of $a$ and $b$ vapour over a flat surface of pure substance.

Equation (1) can be rewritten as

$$\Delta G(n_a, n_b) = -n_a kT \ln \frac{A_{ag}}{A_{al}} - n_b kT \ln \frac{A_{bg}}{A_{bl}} + 4\pi r^2 \sigma,$$

(6)

and taking into account that $\Delta G = 0$ for the virtual monomer we have

$$\Delta G_{cc}(n_a, n_b) = - (n_a - (1 - X)) kT \ln \frac{A_{ag}}{A_{al}} - (n_b - X) kT \ln \frac{A_{bg}}{A_{bl}}$$

$$+ (36\pi)^{1/3} \sigma [(n_a v_a + n_b v_b)^{2/3} - ((1 - X) v_a + X v_b)^{2/3}],$$

(7)

and in the critical conditions

$$\exp \left( - \frac{\Delta G_{cc}^*}{kT} \right) = \exp \left( - \frac{\Delta G^*}{kT} \right) \times \exp \left( \frac{(36\pi)^{1/3} \sigma}{kT} \left[ (1 - X) v_a + X v_b \right]^{2/3} \right),$$

(8)

We now have an expression for $\Delta G$ (equation (7)) which becomes zero for actual monomers of either species. The fact that $\Delta G_{cc}$ is zero also for the virtual monomers is unimportant: $\Delta G_{cc}$ should be interpreted as the difference in the Gibbs free energy between an $(n_a, n_b)$ cluster and a set of $(n_a, n_b)$ actual monomers (gas phase).

The equilibrium distributions of clusters ($N$) are

$$N(n_a, n_b) = F \exp \left( -\frac{\Delta G(n_a, n_b)}{kT} \right)$$

(9)

and in the standard theory

$$F = N_{a0} + N_{b0} + \sum_a \sum_b N_{ab},$$

(10)

where $N_{a0}$ and $N_{b0}$ are the numbers of single molecules of $a$ and $b$ present, and $N_{ab}$ is the number of clusters containing $n_a$, $n_b$ molecules. In the case of the scc-model $F$ represents the total number of monomers. Now we have $\exp (-\Delta G/kT) = 1$ for the clusters $(1, 0)$ and $(0, 1)$, and $N(n_a, n_b) = F$ from equation (9). Therefore we have to make a correction to equation (10) using the Kronecker delta:

$$F_{cc} = (1 - \delta_{0, n_a}) N_{a0} + (1 - \delta_{0, n_b}) N_{b0},$$

(11)

which takes care of the fact that the number of monomer clusters cannot exceed the number of monomers. This expression is needed to calculate the cluster distribution correctly in the scc-model.

The nucleation rate is (Stauffer, 1976)

$$I = R_A V F Z e^{-\frac{\Delta G^*}{kT}},$$

(12)
where $R_A^V$ is an average condensation rate and $Z$ is the Zeldovich factor (for details see Kulmala and Laaksonen, 1990).

The self-consistency correction factor depends on the composition of the critical cluster. The factor as a function of the critical composition is presented in Fig. 1 for the water–ethanol system at two different conditions. In case (a) water activity is 1.0 and ethanol activity is 1.4; in case (b) water activity is 2.0 and ethanol activity 0.75. In both cases temperature is +20°C. The correction factor increases the nucleation rate by more than three orders of magnitude if the mole fraction of ethanol is less than 0.01. In the present calculations we have used the correction factor together with three different theories. In the water–ethanol system the nucleation rates found by different theories [the standard nucleation theory developed by Reiss (1950) and Doyle (1961), the original nucleation theory by Flood (1934) and Volmer (1939) (also called the revised nucleation theory see e.g. Wilemski, 1984) and the explicit cluster model by Laaksonen and Kulmala (1991)] differ from each other so much that the correction factor causes only a minor effect. Generally, all three versions of the classical nucleation theory give different critical compositions under specified conditions, and therefore the factor has a different value for each theory. E.g. in case (b) the mole fraction obtained by the cluster model is 0.34 and by the original theory 0.022, and hence the correction factor for the original theory is more than one order of magnitude higher. The predictions of the explicit cluster model agree well with experiments (see Laaksonen and Kulmala, 1991), and the scc-correction will—in some conditions—slightly improve the agreement.

The nucleation rates (including the hydrates interaction, see Jaecker-Voirol et al., 1984; Kulmala et al., 1991) calculated by the standard classical model and the scc model for the water–sulphuric acid system are presented in Fig. 2 as functions of temperature. The water activity is 0.8 and the acid activity is 0.01. The scc model gives 3–5 orders of magnitude higher nucleation rates than the standard one. At lower temperatures the difference is slightly higher than at moderate temperatures. The actual value of the factor depends on temperature and gas phase activities. At smaller activities (typical for water–sulphuric acid systems) the magnitude of the factor is more significant than at higher activities. The standard binary nucleation theory shows in general much too high nucleation rates compared with experiments in the water–sulphuric acid system (Wyslouzil et al., 1991). The scc-correction tends to increase this discrepancy.

While 3–5 orders of magnitude may be a modest modification in the context of other uncertainties in the classical theory of binary nucleation, it is obvious that the cluster

![Fig. 1. Self-consistency correction factor as a function of mole fraction for the water–ethanol system at +20°C. Solid line: water activity 1.0, ethanol activity 1.4. Broken line: water activity 2.0, ethanol activity 0.75.](image)
The nucleation rate calculated by standard theory (solid line) and scc model (broken line) as a function of temperature for the water–sulphuric acid system. Water activity 0.8; acid activity 0.01.

distribution ought to be written self-consistently, regardless of other aspects of the physical model.

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