Estimation of Saturated Vapor Pressure from Nucleation Data

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Saturated vapor pressure was calculated from the nucleation experimental data using the thermodynamically consistent nucleation theory in which the effect of real gas is considered. The cubic polynomial fit equations of saturation pressure for several substances were obtained based on the calculation. The results of the calculations were compared to those of thermodynamic equilibrium equation and the empirical equation and applied to the predictions of the classical nucleation theory. The results show that the saturation pressures estimated from the nucleation data agree fairly well with those of empirical equations for the substances investigated, and this indicates that the predictions from the classical nucleation theory are close to the experimental data.

Key words: Nucleation data, Saturated vapor, Surface tension

I. INTRODUCTION

Although nucleation theory has been developed for several decades, theoretical predictions of the nucleation rate from the vapor phase to the liquid phase are still not in good agreement with the experimental data. The early homogeneous nucleation theory was developed by Volmer and Weber [1], Farkas [2], and Becher and Döring [3], which has been known as the classical nucleation theory, and has been widely used to predict nucleation rate in phase transition process. For the critical supersaturation measurement, Ktaz and Ostermier [4] found excellent agreement with experiment for methanol, ethanol and other substances by employing a diffusion cloud chamber. However, the measurements of the nucleation rates provide a much more sensitive test of nucleation theory than those of critical supersaturations. In a number of experiments [5–10], the predictions of the classical nucleation theory differ from the experimental data by several orders of magnitude. The reason for such errors in the classical nucleation theory may be attributed to the use of the macroscopic bulk liquid properties (i.e. surface tension) instead of the microscopic properties of the clusters. Then several revised models based on these assumptions were developed [11,12]. Whereas, the predictions of the nucleation rates of these theories are still off by several orders of magnitude in comparison with experiments.

Recently, more robust nucleation theories have been developed. Dillmann and Meier [13] proposed a semiphenomenological model based on Fisher’s droplet theory of condensation, in which the effects of the curvature of cluster and monomer-monomer interactions described by the second virial coefficient on the nucleation model have been considered. Whereas there is an inconsistency within the model, which arises from the fact that the model is to be calibrated against real gas properties, but the chemical potential of a monomer in the supersaturated vapor which was used in the Dillmann-Meier theory is the perfect gas one. This inconsistency was pointed out and revised later by Delale and Meier [14], Ford et al. [15], and Laaksonen et al. [16], Kalikmanov et al. [17]. Unfortunately, the predictions of these revised theories are not better than the Dillmann-Meier theory. For water, Kalikmanov has pointed out that the nucleation rate prediction of the Dillmann-Meier theory is still off by a factor of $10^2$–$10^3$ from the experimental data.

Although efforts have been made to revise the macroscopic properties of the bulk liquid used in the classical nucleation theory, large error is still found in the theoretical prediction of the nucleation rate when compared with experiment. In the classical nucleation theory, the nucleation rate depends on the temperature and the supersaturation which is defined by the ratio of the partial vapor pressure to the saturated vapor pressure. In nucleation rate prediction, the saturated vapor pressure is always calculated by the empirical equation. Therefore, besides the macroscopic properties (i.e. surface tension, density) used in the nucleation theory, what may introduce error to the nucleation rate prediction is the saturated vapor pressure since it is an empirical one. This prompts us to try to use more accurate saturated vapor pressure to fit the theoretical prediction of nucleation rate to experiment.

In this paper, a method of calculation of the saturated vapor pressure from nucleation data is presented. The nucleation theory [18] used is a robust one which is consistently derived from the thermodynamic properties. For comparison, the calculation of saturation pressure from thermodynamic equilibrium equation is also described. The cubic polynomial fit equations for the saturated vapor pressure are obtained and applied to the classical nucleation theory.
II. FORMULA OF THE NUCLEATION THEORY

To evaluate the saturation vapor pressure from the nucleation data, a brief derivation of the nucleation theory is first presented. In the nucleation process, it is assumed that the nuclei created from the supersaturation vapor grow or shrink by a single molecule addition or extraction, and the nuclei and the surrounding vapor have the same temperature $T$. The steady state nucleation rate is therefore given by [19]

$$J = ZD^*c_0(i^*)$$

(1)

where $c_0(i^*)$ is the equilibrium number density of i-mer cluster of critical size. $D^*$ is the rate of monomers impinging on the surface of a critical cluster, which is given by the kinetic expression:

$$D^* = \frac{p_v}{\sqrt{2\pi m_1 kT}} a_0^{1+2/3}$$

(2)

in which $p_v$ is the vapor pressure, $m_1$ is the mass of a single vapor molecule and $a_0 = (36\pi)^{1/3} (\nu_1)^{2/3}$ denotes the mean surface area of a molecule. $Z$ is the Zeldovich or non-equilibrium factor defined by:

$$Z = \frac{-1}{2\pi kT} \left( \frac{\partial^2 \Delta G_i}{\partial n^2} \right)_{i=i}$$

(3)

with $\Delta G_i$ as the Gibbs free energy of the formation of an i-mer cluster. To determine the nucleation rate, the form of the equilibrium number density must be derived. In the followings, the derivation of the equilibrium number density of clusters in a saturated vapor is briefly described.

Firstly we assume that the clusters in the saturated vapor are considered as microscopic monomers, and the mixture of the vapor and cluster is described by the most general type of equation of state

$$\frac{p}{N} = kT + Bp + Cp^2 + \cdots$$

(4)

where $p$ is the pressure of the mixture, $k$ is the Boltzmann’s constant and the coefficients $B, C, \cdots$ are functions of the temperature and are usually called the first, second, \cdots virial coefficients. $N$ denotes the distribution of the monomers of all size containing in the mixture and defined by

$$N = \sum_{i=1}^{\infty} ic_0(i)$$

(5)

Following Wilson [20], the Helmholtz free energy $F$ of all monomers in the mixture is then given by:

$$F(T, V, n) = F(T, V, n)_{\text{ideal}} + \int_0^\infty \left( p - \frac{nRT}{V'} \right) dV'$$

(6)

here $V$ denotes the total volume of the gas, $n$ is the number gram molecules in $V$ and $R$ is the specific gas constant. $F(T, V, n)_{\text{ideal}}$ is the Helmholtz free energy of an ideal gas. All the clusters of i size form a sub-system as an ideal gas gives the Helmholtz free energy by [21]

$$F(T, i)_{\text{ideal}} = c(i)f_f - c(i)kT \left[ 1 - \ln c(i) \right]$$

(7)

per unit volume. In the equation, $f_f$ is the free energy of a single cluster in a unit volume. The corresponding form of the chemical potential of the monomers is given by [20]

$$\mu_v(T, p, n) = \mu_v(T, p, n)_{\text{ideal}} + \int_0^p \left( \frac{\partial V}{\partial n} - \frac{RT}{p'} \right) dp'$$

(8)

where the chemical potential of an ideal gas $\mu_v(T, p)_{\text{ideal}}$ is defined by

$$\mu_v(T, p)_{\text{ideal}} = \mu_s + kT \ln \left( \frac{p}{p_s} \right)$$

(9)

per unit volume, in which $\mu_s$ is the chemical potential of the bulk liquid and saturated vapor, and $p_s$ denotes the saturated vapor pressure over a plane surface. It is well known that the free energy of the vapor has its minimum at the equilibrium condition, it therefore require

$$d \left( \sum_{i=1}^{\infty} F_i - \mu_v N \right) = 0$$

(10)

in which the Lagrangian-multiplier method [21] has been used to take into account the mass conservation, and chemical potential $\mu_v$ acts as the Lagrangian multiplier. The solution of Eq.(10) gives the equilibrium number density of i-mer cluster by

$$c_0(i) = \exp \left( \frac{f_f + H - i\mu_{\text{ideal}}}{kT} \right)$$

(11)

where $H$ represents the contribution of the effect of a real gas and defined by

$$H = \frac{\partial}{\partial c} \left[ \int_V \left( p - \frac{nRT}{V'} \right) dV' \right] - i \int_0^p \left( \frac{\partial V}{\partial n} - \frac{RT}{p'} \right) dp'$$

$$= \left[ kT \ln \left( 1 + \frac{Bp}{kT} \right) + \cdots \right] - i \left( Bp + \cdots \right)$$

(12)

Since the knowledge of the virial coefficients beyond the second term in the equation of state (1) is poorly known, they will be neglected in the following derivation. From Eqs.(11) and (12), the Gibbs formation energy $\Delta G_i$ of i-mer cluster is therefore defined by:

$$\Delta G_i = f_f - i\mu_{\text{ideal}} + kT \ln \left( 1 + \frac{Bp}{kT} \right) - iBp$$

(13)

Following Feder et al. [21] and Wang [18], $f_f$ is suggested by

$$f_f = i\mu_s + \sigma a_0^{2/3} - \tau_1 kT \ln \left( \frac{\varphi^{2/3}}{\lambda^3} \right)$$

$$- \tau_2 kT \ln \left( \frac{\alpha n \varphi^{2/3}}{\lambda^3} \right)$$

(14)
where $\lambda$ is the thermal de Broglie wavelength, $a$ is a geometrical factor and $v_i$ is the volume of a molecule of bulk liquid. $\tau_1$ and $\tau_2$ are the model correctional parameters, which revise the translational and rotational contribution to the free energy of a cluster contained $i$ molecules in a real gas. $\sigma$, the surface tension of the cluster, is given by [22]

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 + 2\delta/r} \quad (15)$$

in which the effect of the curvature of a cluster is considered. $\sigma_0$ denotes the surface tension for planar interface of the bulk liquid, $\delta$ is Tolman’s length and $r$ is the radius of a cluster. Before substituted in the free energy Eq.(14), it is always rearranged based on the Taylor series expansion

$$\sigma = \sigma_0 (1 + \alpha i^{-1/3} + \alpha^2 i^{-2/3} + \cdots) \quad (16)$$

Now combining Eq.(1) with Eqs.(9), (11), (12-14) and (16), this yields the steady state nucleation rate

$$J_s = \frac{p_s a_0}{2\pi \sqrt{m_i kT}} \eta^{i^* - \tau} \sqrt{\frac{2}{9}} \left(1 + 2\tau_i^{i^* - 1/3} + \tau^{2i^* - 2/3}\right) \times \exp \left[i^* \ln S - \theta \left(i^{2/3} + \alpha i^{1/3}\right)\right]$$

$$- \ln \left(1 + \frac{Bp}{kT}\right) + \frac{i^* Bp}{kT}\right] \quad (17)$$

with $\theta$ and $S$, respectively, a dimensionless surface tension and saturation ratio

$$\theta = \frac{\sigma a_0}{kT}, \quad S = \frac{p_c}{p_s} \quad (18)$$

and the auxiliary parameters $\tau$ and $\eta$, respectively, defined by

$$\tau = -\frac{3}{2} \tau_1 + \frac{5}{2} \tau_2 \quad (19)$$

$$\eta = \frac{(\alpha v_i)^{1/3}}{\chi^{(3/2)(\tau_1 + \tau_2)}} \quad (20)$$

Here Eq.(17) is the main equation in this work used to estimate the saturation pressure when nucleation rate, surface tension, partial vapor pressure and total pressure are known, in which the coefficients beyond the second term in the Eq.(16) have been neglected because the contribution of them are very small when compared with the first and second terms. The critical size $i^*$ is determined from the condition equation

$$\left(\frac{\partial \Delta G_i}{\partial i}\right)_{i=i^*} = 0 \quad (21)$$

which represents that $\Delta G_i$ gets its maximum value when an $i$-mer cluster grows into the critical size. Supposing $\tau$ and $\eta$ are known, the behaviors of equation of state (4) and Eqs.(5) and (11) are at the saturation point, i.e. $S = 1$, the surface tension correctional parameters $\alpha$ is therefore implicitly evaluated [18]

$$\frac{p_s}{\eta kT} = \sum_{i=1}^{\infty} \frac{1}{i^{1-\tau}} \exp \left[\frac{iBp}{kT} - \theta \left(i^{2/3} + \alpha i^{1/3}\right)\right] \quad (22)$$

For convergency of the summation series, it requires that $\tau > 2$. Following the Delale-Meier theory [14], $\tau$ is assumed to have the form

$$\tau = 2 + \frac{1}{\varepsilon} \quad (23)$$

where $\varepsilon$ is a three-dimensional universal critical exponent. Finally, $\eta$ is determined from the Eq.(5) at the critical point. Following Wang [18], the values of $\tau$ and $\eta$ are listed in Table I and the properties at the critical point are listed in Table II for several substances.

III. CALCULATION OF THE SATURATION VAPOR PRESSURE FROM THERMODYNAMIC EQUILIBRIUM

Since the vapor pressure is only a function of temperature for univariant equilibrium between vapor phase and the corresponding condensed phase of one component substance, the thermodynamic equilibrium condition is another method to estimate the saturation pressure. For practical application, the equilibrium condition of equilibrium chemical potential for a component in each phase is always introduced. In the present work, the equilibrium condition of the fugacity of each phase is presented. When a closed system only consists of one component vapor and its corresponding condensed phase, the fugacity of the vapor gas $f_v$ is defined by [20]

$$\ln f_v = \ln(y p) + \ln \phi_v \quad (24)$$

where $y$ is the molar vapor fraction. The corresponding equation for the vapor in the condensed phase is written in a similar way

$$\ln f_l = \ln(\gamma x p_{li} \phi_l) + \frac{1}{RT} \int_{p_l}^p \frac{v_l}{p} dp \quad (25)$$

where $f_l$ denotes the fugacity of the vapor in condensed phase, $\gamma$ is the activity coefficient, $x$ is the molar liquid fraction in condensed phase, and $V_l$ is the corresponding molar volume and the fugacity coefficients of both

Table I Model constants $\tau$ and $\eta$ for the substances investigated in this work ($N_c = 6.024 \times 10^{23} p_c / M$)

<table>
<thead>
<tr>
<th>Substances</th>
<th>$\tau$</th>
<th>$\eta / N_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2.208</td>
<td>0.42649</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.162</td>
<td>0.39489</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>2.188</td>
<td>0.43116</td>
</tr>
</tbody>
</table>

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phases $\phi_j$ are defined by

$$\ln \phi_j = \frac{1}{RT} \int_{p}^{p'} \left( \frac{\partial V}{\partial n_j} - \frac{RT}{\rho'} \right) dp'$$

(26)

where $j=v$ or $l$. At equilibrium condition, the fugacity of the vapor is equal to that of the condensed phase. Thus substitute Eq.(26) into Eq.(25) and rearrange to give

$$\ln \frac{yp}{p_s} = \ln \phi_l - \ln \phi_v + \ln(\gamma x) + \frac{1}{RT} \int_{p_s}^{p} V_l dp$$

(27)

Assume that the activity coefficient of vapor in the condensed phase is unity and the vapor is insoluble in the liquid phase, the molar liquid fraction in condensed phase $x$ is considered as unity. In addition, if the liquid is assumed to be incompressible, the volume of the condensed phase is not a function of pressure. Then Eq.(27) can be rewritten as

$$\ln \frac{yp}{p_s} = \ln \phi_l - \ln \phi_v + \frac{V_l(p - p_s)}{RT}$$

(28)

If the equation of state of ideal gas $p = nRT$ is introduced, the fugacity coefficient $\phi_j$ defined by Eq.(26) is equal to one. The saturation pressure is therefore given by

$$\ln p_s = \ln(yp) - \frac{V_l(p - p_s)}{RT}$$

(29)

This equation is used to estimate the saturation pressure in the present work when the vapor and total pressure are known and compared with that calculated from nucleation data. The methods used to derive the relation between vapor pressure and saturation pressure in the mixture of inert noncondensable gas and condensable vapor gas have been presented [23-25], where details of the effect of a real gas on the equilibrium condition, i.e. the monomer-monomer interactions, are described. The saturation pressure calculated from the experimental data of vapor pressure of Carruth using Clausius-Clapeyron equation has been presented by Adams et al. [5]. But the saturation pressures of various substances which are widely used in the nucleation theory are those of empirical equations listed in Table II obtained from Schmeling et al. [26]. Following, the results of saturation pressure estimated from the nucleation data will be compared with those calculated from the thermodynamic equilibrium conditions (Eq.(29)) and empirical equations of Schmeling.

IV. RESULTS AND APPLICATIONS

A. Polynomial fit equation of saturation pressure

If the temperature, partial vapor pressure, total pressure and the nucleation rate are known during the process of steady state nucleation, the saturation pressure of vapor can be calculated by the Eq.(17) together with Eqs.(13), (14), (16), (19-21) and (22). Since the saturation pressure which is estimated from nucleation rate can not be explicitly expressed by other properties existing in the Eq.(17), the calculation process must be run by iterative steps. The results based on the experimental data of Viisanen et al. [27] and Strey et al. [8] for various substances are compared with those calculated from Eq.(29) and the empirical equations listed in Table II.

Figure 1 shows the comparison of the predictions of saturation pressure from nucleation rate using Eq.(17) with those calculated from thermodynamic equilibrium Eq.(29) and empirical equation for water. There is no significant difference between the curves of Eq.(17) and empirical equation. But for the result of the thermodynamic equilibrium Eq.(29), large deviation can be found from those of Eq.(17) and empirical equation due to the neglect of the effect of a real gas, i.e. the monomer-monomer interactions. This indicates that the effect of a real gas on the prediction of saturation pressure is too significant to be neglected. However, the slope of the curve is closed to the other two. For later application, a cubic polynomial fitting equation of the saturation pressure based on the estimation of Eq.(17) from nucleation data of Viisanen et al. [27] is given by

$$\ln p_s = -92.79152 + 0.91574T - 0.00289T^2 + 3.30333 \times 10^{-6}T^3$$

(30)

Figure 2 and Figure 3 display that the saturation pressures calculated from the experimental data of nucleation rate of Strey [8] for two alcohols, methanol and $n$-propanol, are compared with those of Eq.(29) and empirical equation. Similar to the result of water, the result of Eq.(29) appears to be larger than those of the other two. The prediction of saturation pressure from nucleation data shows small difference from the empiri-
TABLE II Thermodynamic properties of various substances molar mass M (in g/mol), saturation pressure $p_c$ (in Pa), surface tension $\sigma_0$ (in dyn/cm), liquid density $\rho_c$ (in g/cm$^3$), second virial coefficient $B$ (cm$^3$/mol), the properties at the critical point: $T_c$ (in K), $p_c$ (in Pa), $\rho_c$ (in g/cm$^3$). The temperature-dependent quantities are given as functions of absolute temperature $T$ (in K), of reduced temperature $T_r = T/T_c$. (Consult from Dillmann and Meier [13])

<table>
<thead>
<tr>
<th>Substance</th>
<th>$M$</th>
<th>$T_c$</th>
<th>$p_c$</th>
<th>$\rho_c$</th>
<th>$\sigma_0$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.015</td>
<td>647.13</td>
<td>2.2060 x 10^8</td>
<td>0.323</td>
<td>93.6635 + 0.0091333T - 0.0002757T^2</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>32.042</td>
<td>512.64</td>
<td>8.092 x 10^7</td>
<td>0.272</td>
<td>24.23 - 0.09254(T - 273.15)</td>
<td></td>
</tr>
<tr>
<td>n-Propanol</td>
<td>60.069</td>
<td>536.78</td>
<td>5.170 x 10^7</td>
<td>0.275</td>
<td>25.28 - 0.08394(T - 273.15)</td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 2** Comparison of the saturation pressure for methanol plotted as $\ln p_s$ vs. temperature.

**FIG. 3** Comparison of the saturation pressure for n-propanol plotted as $\ln p_s$ vs. temperature.

cal equation in the high temperature region of the temperature range investigated for methanol or in the low temperature region for n-propanol. The slope of the curve of Eq.(17) is slightly larger than that of empirical equation, so that there must be a crossing point of these two curves somewhere, i.e. at about 239 K for methanol and 290 K for n-propanol on the abscissa. These are the turning points which reverse the accuracy of the theoretical predictions of nucleation rate along the two curves. The cubic polynomial fitting equation of the saturation pressure based on experimental data
of nucleation rate for methanol is written as
\[
\ln p_s = -62.11089 + 0.559777T - 0.001671T^2 \\
+ 1.57307 \times 10^{-6}T^3
\] (31)
and the corresponding fitting equation of the saturation pressure for \(n\)-propanol is given by
\[
\ln p_s = -75.71084 + 0.647197T - 0.00147T^2 \\
+ 1.1876 \times 10^{-6}T^3
\] (32)
These polynomial fitting equations of the saturation pressure based on the experimental data will be applied to the classical nucleation theory as following.

B. Applied to the classical nucleation theory

It is well known that the theoretical prediction of nucleation rate from the classical theory is off by a factor of several orders of the magnitude from experimental data. The reason of the failure in the prediction of the nucleation rate from classical theory is various. However, the saturation pressure is also a significant parameter which affects the nucleation rate dramatically. Now the classical nucleation theory together with saturation pressure Eqs.(30), (31) and (32) for water, methanol and \(n\)-propanol, the theoretical predictions of the nucleation rate are compared with experimental data of Viisanen et al.[27] and Strey et al. [8]. The theoretical results based on the empirical equation of saturation pressure were listed in Table II, shown in Fig.4, Fig.5 and Fig.6. It can be found that small change in the saturation pressure made sensitive change in nucleation rate. The results of nucleation rate using the saturation pressure Eqs.(30) or (31) for water or methanol have better agreement with experiment. Unfortunately, the result of nucleation rate using Eq.(32) for \(n\)-propanol is worse than that using the empirical equation. This error maybe stem from the calculation of vapor pressure during the process of estimation of the saturation pressure by Eq.(18), because this definition of saturation ratio is only suitable for the vapor molecules exist as monomers. Question would arise when it is used for the associating vapor like the lower alcohols. For this reason, the experimental data for methanol has been calibrated using the law of mass action by Strey et al. [8], but not for \(n\)-propanol, so that large error can be found in the result of \(n\)-propanol.
V. CONCLUSION

The saturated vapor pressures calculated from experimental data of nucleation rate are described for various substances, and the corresponding cubic polynomial fitting equations for saturation pressure are also presented and applied to classical nucleation theory. The nucleation theory used to calculate the saturation pressure from experimental data is the thermodynamically consistent one in which the effect of a real gas is considered. The values of the model correction parameters are listed in Table I. The results of the saturation pressure have no significant difference from the empirical equation. However, when the cubic polynomial fitting equations of the present work are applied to the classical nucleation theory, theoretical predictions of nucleation rate give better agreement with the experiment. The calculations of saturation pressure from the fugacity equilibrium of ideal gas is also described. The results show large deviation from those of the present work and empirical equations. Whereas, it can correctly describe the slopes of the curves of saturation pressure. This indicates that the effect of the real gas is important in the calculation of the saturated vapor pressure.

VI. ACKNOWLEDGMENTS

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