VAPOUR–TO–LIQUID NUCLEATION: NUCLEATION THEOREMS FOR NONISOTHERMAL–NONIDEAL CASE

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Vapour–to–liquid nucleation: Nucleation theorems for nonisothermal–nonideal case

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Homogeneous vapour–to–liquid nucleation, a basic process of aerosol formation, is often considered as a type of nucleation phenomena, while most treatment of the subject introduce several simplifying assumptions (ideal gas phase, incompressible nucleus, isothermal kinetics, size-independent surface free energy…). During last decades, nucleation theories have provided new insights into properties of critical nuclei facilitating direct comparison between laboratory experiments and molecular simulations. These theories are, despite of their generality, often applied in forms where the aforementioned assumptions are made. Here we present forms of nucleation theories that explicitly take into account these effects and allow direct estimation of their importance. Only assumptions are Arrhenius-type kinetics of nucleation process and exclusion carrier gas molecules from the critical nucleus.

Nonideal gas is described by a virial equation of state, \( P = p_v + p_g = \rho kT (1 + B \rho) \), where the total pressure \( P \) is given by partial pressures of carrier gas (g) and vapour (v), \( \rho \) is density and \( B = y_1 B_c + 2 y_1 y_2 B_g + y_2^2 B_v \) is the total second virial coefficient with pure component and cross virial coefficients \( B_c \), \( B_g \), and \( B_v \), respectively, and \( y_i = p_i/P \). For the nonisothermality correction, we follow zeroth-order approximation of Barrett et al. (1993, 2008), but instead of the capillarity approximation, we identify surface free energy contributions in terms of excess enthalpy \( H_g \), i.e. difference between enthalpies of similar clusters immersed in supersaturated vapour and bulk liquid that can be obtained using the second nucleation theorem (cf. Ford, 1997). Resulting equations for number of molecules in the cluster \( n \), \( H_g \), and mean molecular volume \( v \) inside critical nucleus (after neglecting minor dependencies of specific isochoric heat capacities on partial pressures \( p_i \) in terms of experimental nucleation rate \( J = \lambda T p_v p_g \)) and equilibrium properties of carrier gas, condensing vapour and bulk condensed phase are

\[
\begin{align*}
\frac{d}{dt} \ln S &= \frac{kT}{p_v} + \frac{4T(Q + \tilde{c}_v)}{S} + \frac{\partial \ln \nu}{\partial T} \left[ \frac{kT}{p_v} - \nu + \frac{(p_v + p_g) \tilde{B}_c + p_v (B_g - 2 B_v)}{p^2} \right] - 1 / (1 - vp) \\
H_g &= kT \left[ 1 - \frac{L}{p_v \Delta \nu} + T \left( \frac{\partial \ln J}{\partial T} \right)_{p_v, p_g} - \frac{n - 1}{1 - vp} \left[ \frac{y_1^2 B_c + y_1 y_2 B_g + y_2^2 B_v}{2 \frac{d B_v}{dT}} \right] + \frac{B_L}{\Delta \nu} - \frac{\partial \tilde{c}_v(1 + \lambda)}{\partial T} - \frac{\partial (Q + \tilde{c}_v^2)}{\partial T} \right] \\
&- \frac{B_L}{\Delta \nu} - \frac{\partial \tilde{c}_v(1 + \lambda)}{\partial T} - \frac{\partial (Q + \tilde{c}_v^2)}{\partial T} \left[ \frac{\partial \tilde{c}_v(1 + \lambda)}{\partial T} \right] \\
\nu &= \frac{kT(1 - vp)}{1 - n} \left( \frac{\partial \ln J}{\partial T} \right)_{p_v, p_g} + \frac{p_v^2 B_c + 2 p_v (p_g + 2 p_v) B_g - 2 p_v p_g B_v}{p^2} - \frac{\tilde{c}_v(1 + \lambda)}{\tilde{c}_v(1 + \lambda) + (Q + \tilde{c}_v^2)} \frac{\partial (Q + \tilde{c}_v^2)}{\partial \rho} \\
&+ \frac{\tilde{c}_v(1 + \lambda)}{\tilde{c}_v(1 + \lambda) + (Q + \tilde{c}_v^2)} \frac{\partial (Q + \tilde{c}_v^2)}{\partial \rho}
\end{align*}
\]

Here \( S = p_v/p_g \), \( p_v \) is the equilibrium vapour pressure, \( L \) is the molecular enthalpy of condensation, and \( Q \) is the net energy released to gas phase due to condensation of a vapour molecule, and \( \lambda \) and \( \tilde{c}_v \) are as given by Barrett (2008). By applying Eqs. (1)–(3), it is possible to extract properties of critical nuclei without assumptions concerning their physical state. Under ideal–isothermal conditions with \( \Delta \nu = 1/\rho - v \approx kT p_v \), Eqs. (1) and (2) simplify to “standard” forms of first and second nucleation theorems, while when \( y_g \to 1 \), Eq. (3) recovers form obtained first by Oxtoby & Laaksonen (1995).

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