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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 example 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 theorems have provided new insights into properties of critical nuclei facilitating direct comparison between laboratory experiments and molecular simulations. These theorems are, despite of their generality, often applied in forms where the aforementioned assumptions are made. Here we present forms of nucleation theorems 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), ρ is density and $B = y_v^2 B_v + 2y_v y_g B_{vg} + y_g^2 B_g$ is the total second virial coefficient with pure component and cross virial coefficients B_v, B_g, and B_{vg}, 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_x, *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_x, 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 $J = J(T,p_v,p_g)$ and equilibrium properties of carrier gas, condensing vapour and bulk condensed phase are

$$n = \left\{ \frac{kT}{p_v} \left[\left(\frac{\partial \ln J}{\partial \ln S} \right)_{T,p_g} + \frac{4T(Q+\hat{c}_{bv})}{3[\hat{c}_{bv}(1+\lambda)+(Q+\hat{c}_{bv})^2]} \left(\frac{\partial \ln v}{\partial T} \right) \right] \middle/ \left[\frac{kT}{p_v} - v + \frac{(P^2+p_g^2)B_v + p_g^2(B_g-2B_{vg})}{P^2} \right] - 1 \right\} \middle/ (1-v\rho) \quad (1)$$

$$H_x = kT \left\{ \left(1 - \frac{L}{p_e \Delta v} \right) + T \left[\left(\frac{\partial \ln J}{\partial T} \right)_{p_v,p_g} - \frac{n-1}{1-v\rho} \left\{ P \left[y_v^2 \frac{dB_v}{dT} + y_v y_g \left(3\frac{dB_{vg}}{dT} - \frac{dB_g}{dT} \right) + y_g^2 \left(2\frac{dB_{vg}}{dT} - \frac{dB_g}{dT} \right) \right] \right. \right.$$
$$\left. \left. - \frac{B_v L}{\Delta v} - p_e T \frac{dB_v}{dT} \right\} - \frac{\hat{c}_{bv}(1+\lambda)}{\hat{c}_{bv}(1+\lambda)+(Q+\hat{c}_{bv})^2} \frac{\partial}{\partial T} \left[\frac{(Q+\hat{c}_{bv})^2}{\hat{c}_{bv}(1+\lambda)} \right] \right] \right\} \quad (2)$$

$$v = \frac{kT(1-v\rho)}{1-n} \left\{ \left(\frac{\partial \ln J}{\partial p_g} \right)_{T,p_v} + \frac{p_v^2 B_v + 2p_g(p_g+2p_v)B_{vg} - 2p_v p_g B_g}{P^2} - \frac{\hat{c}_{bv}(1+\lambda)}{\hat{c}_{bv}(1+\lambda)+(Q+\hat{c}_{bv})^2} \frac{\partial}{\partial p_g} \left[\frac{(Q+\hat{c}_{bv})^2}{\hat{c}_{bv}(1+\lambda)} \right] \right\} \quad (3)$$

Here $S = p_v/p_e$, p_e 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 λ and $\hat{c}_{bv}$ 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 $\Delta v = 1/\rho - v \approx kT/p_v$, 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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