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ON THE NON-EQUILIBRIUM FACTOR FOR NUCLEATION RATES

by

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The series of approximations and somewhat tedious analyses generally undertaken to evaluate the non-equilibrium factor[1] for nucleation of phase transformations is easily replaced by a direct and more accurate evaluation. Present analysis is based on the Becker-Doering[2] approach and will be considered for nucleation of a solid phase β from a one-component liquid α.[3]

The Gibbs free energy for the formation of an embryo β_i containing i molecules is

$$\Delta G_i = 4\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} i^{2/3} \gamma + i\Omega \Delta G_v = A\, i^{2/3} + Bi \qquad (1)$$

where γ is the free energy per unit interfacial area, ΔG_v is the change in free energy upon formation of a unit volume of the embryo and Ω is the volume per molecule of the embryo. ΔG_i exhibits a maximum value of $\Delta G_i{}^*$ dicated by $\left(\frac{\partial \Delta G_i}{\partial i}\right)_{i^*} = o$. Embryos for which $i < i^*$ grow by a series of unimolecular reactions, $\alpha_1 + \beta_i \rightleftarrows \beta_{i+1}$ and nucleation occurs when $\alpha_1 + \beta_{i^*} \rightarrow \beta_{i^*+1}$. As the β_{i^*+1} nuclei are withdrawn at the rate $\dot{N}$ per unit volume per second a steady state flux, $J_{i \rightarrow i+1}$ of the promotion of i to the i + 1 nuclei takes place. A diagram of the free energies involved in the addition of one molecule of the liquid phase to the solid embryo is given in Fig. 1 where g_m^+ is the free energy of activation for diffusive motion of an atom at the surface of an embryo. At the steady state therefore

$$J^{net}_{i\ i+1} = \dot{N} = n_i \left[4\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} i^{2/3} \frac{\lambda}{\Omega}\right]\left[\nu\, e^{-g^{\dagger}_{m}/kT}\right] e^{-\frac{1}{kT}\left(\frac{\Delta G_{i+1} + \Delta G_i}{2} - \Delta G_i\right)}$$

$$- n_{i+1}\left[4\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} (i+1)^{2/3} \frac{\lambda}{\Omega}\right]\left[\nu\, e^{-g^{\dagger}_{m}/kT}\right] e^{+\frac{1}{kT}\left(\Delta G_{i+1} - \frac{\Delta G_{i+1} + \Delta G_i}{2}\right)} \tag{2}$$

where λ is the molecular diameter, ν is the jump attempt frequency, n_i is the steady state number of embryos per unit volume containing i molecules, and the first term in square brackets gives the number of liquid molecules adjacent to the i th embryo. Under equilibrium conditions the net flux would be zero and invoking the concept of microbalance, we find

$$n^e_i\ i^{2/3}\, e^{-\frac{1}{kT}\left\{\frac{\Delta G_{i+1} - \Delta G_i}{2}\right\}} = n^e_{i+1}\ (i+1)^{2/3}\, e^{\frac{1}{kT}\left\{\frac{\Delta G_{i+1} - \Delta G_i}{2}\right\}} \tag{3}$$

Introducing Eq. 3 on the right hand term of Eq. 2, rearranging the terms and multiplying both sides of the equality by $(n^e_i)^{-1}$ gives

$$\frac{\dot{N}\ e^{\frac{1}{kT}\left(\frac{\Delta G_{i+1} - \Delta G_i}{2}\right)}}{4\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} i^{2/3} \frac{\lambda}{\Omega}\ e^{-g^{\dagger}_{m}/kT}\ n^e_i} = \frac{n_i}{n^e_i} - \frac{n_i + 1}{n^e_i + 1}\ , \tag{4}$$

where $n^e_i = n_1\, e^{-\Delta G_i/kT}$. Because critical nuclei are being removed, $\frac{n_{i^*+1}}{n^e_{i^*+1}} \simeq o$ and also since $\frac{n_1}{n^e_1} \simeq 1$ we find that

$$\sum_{i=1}^{i^*}\left[\frac{n_i}{n^e_i} - \frac{n_{i+1}}{n^e_{i+1}}\right] \simeq 1.$$

Furthermore Since $\sum_{i=2}^{i^*} n_i \ll n_1$, it follows that

$$\dot{N} = 4\pi\left(\frac{3\Omega}{4\pi}\right)^{2/3} i^{*2/3}\, n_1 \frac{\lambda}{\Omega}\, \nu e^{-g^+ m/kT}\, e^{-\frac{\Delta G_{i^*}}{kT}} \qquad \phi = \dot{N}^e \phi$$

where the non-equilibrium factor is

$$\phi = \left[\sum_{i=1}^{i^*} \frac{e^{-\frac{1}{kT}\left(G_{i^*} - \frac{\Delta G_{i+1} + \Delta G_i}{2}\right)}}{(i/i^*)^{2/3}}\right]^{-1} \tag{5}$$

By direct evaluation of the sum we obtain

$$\phi = \left(\frac{2.22}{3\pi kT}\frac{\Delta G_{i^*}}{i^{*1.92}}\right)^{1/2} = \left(-\frac{1.11\,\Omega\,\Delta G_v}{3\pi kT\; i^{*0.92}}\right)^{1/2} \tag{6}$$

whereas the usual value reported by approximate integration is[1]

$$\phi = \left(\frac{\Delta G_{i^*}}{3\pi\, kT\; i^{*2}}\right)^{1/2} \tag{7}$$

The nominal agreement of the present results as depicted in Fig. 2 attests to the accuracy of the previously made approximations.

Although the differences in the present and earlier results as shown by equations (6) and (7) are trivial in terms of the other more important issues regarding nucleation, the direct summation has substantial pedagogic advantages.

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References

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2. R. Becker and W. Doering, Ann. Phys. (5) 24, 79 (1935).

3. D. Turnbull and J. C. Fisher, J. Chem. Phys. 17, 71 (1949).

Figure Captions:

1. Free energy representation for the reaction $\alpha_1 + \beta_i = \beta_{i+1}$

2. Plot of ϕ vs $\left(\frac{2.22}{3\pi kT}\frac{\Delta G_{i^*}}{i^{*1.92}}\right)^{1/2}$ for various values of i*. Solid line represents Eq. 6.

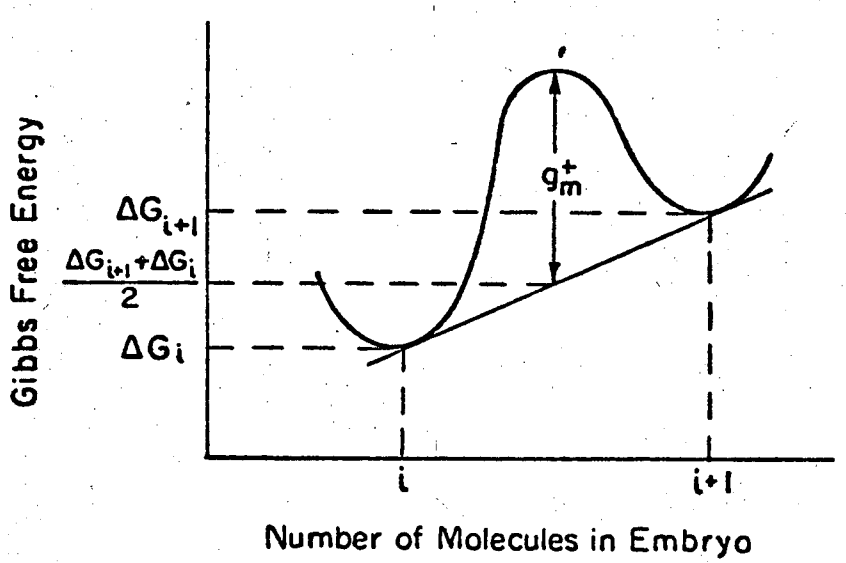

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Fig. 1

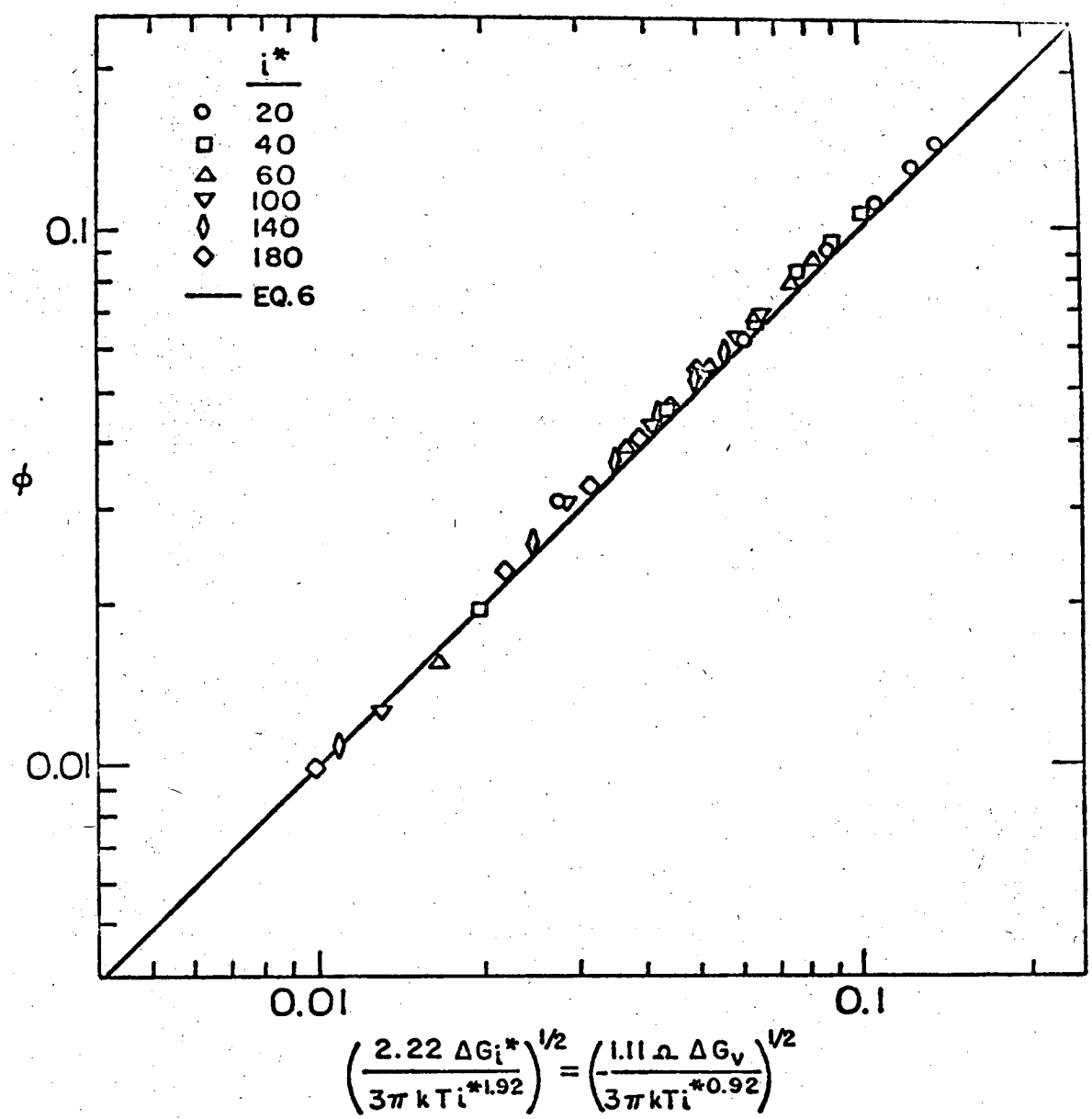

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Fig. 2

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