

## SIMILAR EQUATIONS FOR RAIN AND ICE EMBRYOS

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**ABSTRACT:** Classical nucleation theory goes back to the early work by Lord Kelvin, Josiah Willard Gibbs and Max Volmer. A very good equation, of the form  $J = A \exp(K)$ , was given by Blander/Katz (1975) for Bubble Nucleation in Liquids. Surface tension for polymer solutions comes from a workup by Siow/Patterson (1973). Jennings (2014) combined them to get a formula and then extended it to an equation, Jennings (2021), predicting the dew point (onset of rain) for a cloud. Pruppacher/Klett (1997) have their equation for rain embryos,  $J = C \exp(D)$ , in the form of other homogeneous nucleation equations. The author maintains that these equations follow the same mathematics, so one can conclude that  $(d \ln C / dD) = \text{small}$  as well as the similar form from complicated mathematics showing  $(d \ln A / dK) = 1/(6K) = -0.26\%$  in Jennings (2020). It is known that  $\sigma$ , the surface tension, dominates in calculating J, the nucleation rate, for both processes. In this paper the raindrop and ice germ equations will be presented. Young (1993) has an equation for the homogeneous freezing rate.

### I. INTRODUCTION

A nucleation equations is of the form  $J = C \exp(D)$ , for the raindrop embryo formula. C is constant with respect to  $\exp(D)$  and this is shown by forming.

$$\ln J = \ln C + D \quad (1)$$

$$d \ln J / dT = d \ln C / dT + dD / dT \quad (2)$$

$$\text{suppose } (d \ln C / dT) / (dD / dT) \text{ is small} \quad (3)$$

Then that proves that D can be taken as a constant. Both C and D are a jumble of multiplied terms and J is fully presented in Pruppacher/Klett (1997) pages 198, 202. The author has found out the values of all the unknowns at 0 degrees Centigrade and derived a new formula by differentiating D.

### II. RESULTS

The mathematics follows Jennings' (2012) paper on polymer solutions. Here is the Pruppacher/Klett (1997), page 202, equation (4) here, for raindrop embryos.

$$J = \alpha_c / \rho_w \left( (2N_A^3 M_w \sigma_{w/v}) / \pi \right)^{1/2} (e_{\text{sat}, w} / RT)^2 S_{v, w} \exp(-\Delta F_g / kT) \quad (4)$$

And, here is their equation for  $\Delta F_g$ , page 198.

$$\Delta F_g = (16 \pi M_w^2 \sigma_{w/v}^3) / (3 [RT \rho_w (\ln S_{v, w})]^2) \quad (5)$$

Notice, Eq. (5) inserted in Eq. (4) is of the form  $J = C \exp(D)$ . On page 202, they say that uncertainties in C are insignificant with respect to uncertainties in  $\Delta F_g$ . So, proceeding, we may assume  $D = \text{constant}$  and take  $dT/d\phi_2$ , after solving for T, where  $D = -\Delta F_g / kT$ . We obtain,

$$D = - (16 \pi M_w^2 \sigma_{w/v}^3) / (3 [RT \rho_w (\ln S_{v, w})]^2 kT) \quad (6)$$

or

$$T^3 = - (16 \pi M_w^2 \sigma_{w/v}^3) / (D 3 [R \rho_w (\ln S_{v, w})]^2 k) \quad (7)$$

Going further,

$$3T^2 dT/d\phi_2 = - ((16 \pi M_w^2) / (3D[R\rho_w]^2 k)) (d (\sigma_{w/v}^3 (\ln S_{v,w})^{-2})/d\phi_2) \quad (8)$$

And Eq. (8) applies to the critical droplet of rain and note that  $\rho_w$  is constant as water is incompressible. The result is.

$$3T^2 dT/d\phi_2 = - ((16 \pi M_w^2) / (3D[R\rho_w]^2 k)) (3\sigma_{w/v}^2 (\ln S_{v,w})^{-2} d\sigma_{w/v}/d\phi_2 - 2 \sigma_{w/v}^3 (\ln S_{v,w})^{-3} (1/S_{v,w}) dS_{v,w}/d\phi_2) \quad (9)$$

In order to get  $dS_{v,w}/d\phi_2$ , we have to realize that  $S_{v,w} \equiv RH(\%) \times 100 = P_{H_2O}/P^*_{H_2O}$ , where  $P_{H_2O}$  = water vapor pressure in the surrounding gas and  $P^*_{H_2O}$  = equilibrium vapor pressure of water.  $P^*_{H_2O}$  is a function of temperature only, independent of  $\phi_2$ , the volume fraction of surrounding gas. We have to assume the surface of the droplet embryo follows Raoult's Law:  $P_{H_2O}(0)$  is an intensive quantity,  $\phi_{2s}$  is vanishingly small on the surface of the droplet and matters the most, as surface effects are important for the equilibrium vapor pressure, viz,  $P_{H_2O} = P_{H_2O}(0)(1 - \phi_{2s})$ . This is patterned after Jennings (2012), Eq. (5), there. So, the term with  $dS_{v,w}/d\phi_2$  drops out because  $P_{H_2O}(0)$  and  $P^*_{H_2O}$  pull out from the differential to leave  $d(1 - \phi_{2s})/d\phi_2$ , which is negligible as in Jennings (2012) page 128:

$\partial\phi_{2s}/\partial\phi_2 \approx 10^{-38}$  for MW 2000 and even less for higher MW. That leaves (10).

$$3T^2 dT/d\phi_2 = ((- 16 \pi M_w^2) / (3D[R\rho_w]^2 k))(3\sigma_{w/v}^2 (\ln S_{v,w})^{-2} d\sigma_{w/v}/d\phi_2) \quad (10)$$

Or, simplifying, we have.

$$dT/d\phi_2 = (T/\sigma_{w/v})(d\sigma_{w/v}/d\phi_2) \quad (11)$$

### III. DISCUSSION

Now, the author maintains that  $d\sigma/d\phi_2$  in Jennings' (2012), Eq. (9) is the same kind of thing as  $d\sigma_{w/v}/d\phi_2$ , as the droplet embryo is the new phase, the pure water droplet. Jennings (2012), Eq. (9), is here as (13) with  $\lim \phi_2 \rightarrow 0$ , but  $\lim \phi_2 \rightarrow 0$  is dropped and transformed to give (14) because the polymer solution data is linear for 2000 and 4000 MW, Jennings/Middleman (1985): data is paramount. Furthermore,  $\sigma_{w/v}$  is in (14) instead of  $\sigma$  as Raoult's Law is assumed to apply in the rain germ.

$$\lim \phi_2 \rightarrow 0 \quad d\sigma / d\phi_2 = kT/ra \quad (13)$$

$$d\sigma_{w/v} / d\phi_2 = kT/ra \quad (14)$$

Following Jennings (2012),  $r$  = molar volume of surrounding gas/molar volume of water in water germ =  $(M_v/\rho_v)/(M_w/\rho_w)$ . So, formula (11), inserting (14) and  $r$ , becomes (15).

$$dT d\phi_2 = (kT^2/\sigma_{w/v}a) ((M_w/\rho_w)/(M_v/\rho_v)) \quad (15)$$

The author has no idea what Eq. (15) is good for and is aware of no data to test it. The corresponding equation in Jennings (2012), (16) there, differs by a factor of three but a possible explanation is that Jennings (2012) is concerned with polymer solutions explosively superheating and this paper is concerned with water vapor coalescing into raindrops or ice germs interfacing with water.

### IV. CONCLUSION

For classical nucleation theory there is a prefactor and an exponential part. The exponential part dominates and the surface tension appears as  $\sigma^{3/2}$  in the prefactor and  $\sigma^3$  in the exponent. The original data on polymer solutions for Jennings/Middleman (1985) showed a linear rise in superheat with weight fraction and inversely proportional to molecular weight polystyrene in cyclohexane.

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**SELECTED NOMENCLATURE**

- a surface area of water molecule
- $e_{s,w}/e_{s,i} = S$  saturation ratio
- k Boltzmann constant
- $M_v$  molecular weight of surrounding gas
- $M_w$  molecular weight of water
- MW molecular weight
- $N_I$  number density for ice at 0°C
- $P_{H2O}$  actual vapor pressure of water in gas surrounding the raindrop embryo
- $P_{H2O}(0)$   $P_{H2O}$  when  $\phi_{2S} = 0$
- $P^*_{H2O}$  equilibrium vapor pressure of water
- r ratio of molar volume of surrounding gas to molar volume of water in water germ
- R universal gas constant
- RH relative humidity as %
- $S_{v,w}$  saturation ratio
- T absolute temperature of cloud
- $\rho_v$  density of surrounding gas
- $\rho_w$  density of water, incompressible
- $\sigma$  polymer solution surface tension
- $\sigma_{IL}$  surface tension of ice against water
- $\sigma_{w/v}$  surface tension of water against surrounding gas
- $\phi_2$  volume fraction of surrounding gas
- $\phi_{2S}$  surface volume fraction of non-water gas on rain germ

**APPENDIX**

For a cloud forming ice we have the formula (A) Young (1993), page 76.

$$J = 1 \times 10^{28} \exp \left\{ - 16 \pi \sigma_{IL}^3 / 3 (kT)^3 [N_I \ln (e_{s,w}/e_{s,i})]^2 \right\} \quad (A)$$

Applying the same treatment as in the body of the text, we have (B), which compares with (11).

$$dT/d\phi_2 = (T/ \sigma_{IL}) (d\sigma_{IL}/ d\phi_2) \quad (B)$$

The exponents in (4) and (A) have a similarity. For the ice germ, (13) doesn't apply as it is a solid-liquid interface. Thus, in a cloud, the result is a factor 3 different in the exponent from polymer solution superheating.

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