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Classical Nucleation and Lattice Model Unite

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

Classical nucleation theory predicts the limit of superheat of liquids quite well. To come up with an equation for the limit of superheat of polymer solutions, the lattice model for polymer solutions was used to give the surface tension of polymer solutions. A formula for bubble nucleation in polymer solutions was derived by Jennings with the precursor equation $\ln A/dK=1/(6K)$ where $J=AexpK$ gives the nucleation rate for liquids. The aim of this paper was to show that the precursor equation holds for monomer in the polystyrene-cyclohexane system. Thus, the precursor equation is true for all molecular weight polymer. This happens because the surface tension of polystyrene is significantly more than cyclohexane and the influence of the surface tension dominates.

Keywords: Polymer solutions; classical nucleation theory; surface tension; limit of superheat; lattice model.

NOMENCLATURES

a : Surface area of solvent molecule

A : Prefactor

B : Coefficient

d : Density of liquid

J : Nucleation rate

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- k : Boltzmann constant
- K : Exponent
- M : Molecular weight of liquid
- MW_i : Molecular weight: solvent 1, polymer 2
- P_e : Equilibrium vapor pressure
- PL : Ambient pressure
- P_v : Vapor pressure
- T : Temperature Kelvin of limit of superheat of solution
- T_o : Limit of superheat of solvent in Kelvin
- w : Weight fraction polymer
- δ : Poynting correction factor
- ΔT : Rise in superheat in Centigrade = $T - T_o$
- σ : Surface tension

1. INTRODUCTION

Classical nucleation theory goes back to Josiah Willard Gibbs where increasing entropy and decreasing energy give way to an emerging bubble forming aided by the rise in temperature known as the limit of superheat. Flory and Huggins theory provided an understanding of the behavior of a polymer solution and Prigogine and Marechal [1] derived equations for the surface tension of polymer solutions, following Flory/Huggins. Other attempts at solving the problem of bubble nucleation in polymer solutions were complicated and had no good data, for example (in addition to Prud'homme/Gregory [2]), Yarin, et al. [3] said bubble growth is controlled by momentum transfer and diffusion or Han and Han [4] did a lengthy theoretical study that was very involved. My theory offers simple equations that are exact and predict the linearity in weight fraction and the trend in molecular weight polymer. Conceivably, the equations and results in this study could be applied toward fuel burning where the limit of superheat is present and affects the efficiency of thrust of a rocket or high performance racecar.

2. THEORY

This paper is based on a highly cited paper by Blander and Katz [5] and another paper by Siow and Patterson [6]. Jennings joined these streams of thought for the first time in 2012 by coming up with this formula for the limit of superheat as polymer $w_2 \rightarrow 0$.

$$\lim_{w_2 \rightarrow 0} \partial T / \partial w_2 = (MW_1 / MW_2) (3kT_o^2 / \sigma a) \quad (1)$$

Mathematically, Eq. (1) is only true in the limit of zero weight fraction polymer in the solution because of the limitation in getting the surface tension. However, the actual Jennings and

Middleman [7] data shows straight vectors in (w,T) space for lower molecular weight. In Jennings' [8] paper, the [9] equation (1) was expanded because of that. Here is the expanded equation.

$$\Delta T = 3kT_o^2 w MW_1 / \sigma a MW_2 \quad (2)$$

So, the question is, What led to Eq. (2)? It is Eq. (3) from Jennings [9] paper.

$$\lim_{w_2 \rightarrow 0} (\partial \ln A / \partial w_2) / (\partial K / \partial w_2) = 1 / (6K) \quad (3)$$

Another way to write (3) is (4).

$$d \ln A / dK = 1 / (6K) \quad (4)$$

A and K are found in the equation (Z) in the APPENDIX, Blander and Katz's formula for bubble nucleation in liquids: A is the prefactor in (Z) and K is the exponent in (Z). In APPENDIX is sketched out my method for checking the validity of (4) for monomer, that is $r = 1$, where r is the ratio of the molar volume of polymer to the molar volume of solvent. Furthermore, (4) has a well-defined integration constant that was calculated in Jennings [10] article. See the same Jennings [10] article for details pertaining to this derivation and Jennings [9] for all of the values to input in the equations in APPENDIX. Polystyrene-cyclohexane is a model system, so Eq. (4) is proposed as a general equation when the surface tension of the polymer is significantly greater than the surface tension of the solvent.

3. METHODOLOGY

In the early 1980s, Jennings and Middleman collected data on liquid \rightarrow gas nucleation in polymer solutions that was published in 1985. In early 2020 the study was complete, except direct

calculation revealed that the surface tension is so influential that only the surface tension terms matter and so the 2012 equations are true for any degree of polymerization, that is $r = 1$ up to $r = \infty$, for the polystyrene-cyclohexane model system.

4. RESULTS AND DISCUSSION

Unfortunately, there is no known data, except a lone styrene point in the 1985 paper, but plugging in the numbers gave a result that was off by about a factor of 10. There is data on polystyrene/benzene gathered by Prud'homme and Gregory [2], but it does not agree with Eq. (2) at all. The beauty of this entire study from Fall 1980 to now is that it shows how the very successful classical nucleation theory unites with the lattice model for polymer solutions. The author knows of no one else who used Siow and Patterson's [6] theory to solve this problem and the others who attempted it had complicated equations.

5. CONCLUSIONS

The author first started on this project in 1980 and feels that this paper concludes it. It is remarkable how influential the surface tension is in bubble nucleation. Possibly this paper will get noticed and lead others to explore the ramifications of the uniting of what started with Gibbs and Flory/Huggins.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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APPENDIX

Part 1

Here, we establish $\ln A/dK=1/(6K)$ for $r = 1$.

This is the Proof of $\ln A/dK = 1/(6K)$ for all pure liquids $J = A \exp K$, where

J = nucleation rate, A = prefactor and K = exponent.

from Blander and Katz classical nucleation theory liquid→gas. Siow and Patterson present equations for the surface tension of polymer solutions.

The starting equations are from

1) Blander and Katz (Z) and 2) Siow and Patterson (A) and (B).

See JH Jennings, International Journal of Thermodynamics article 2012.

page 127-128. Everything here is done as $\phi_2 \rightarrow 0$ and $T \rightarrow T_0$.

Note that ϕ_2 and T are orthogonal.

$$J \approx 3.73 \times 10^{35} (d^2 \sigma / M^3 B)^{1/2} \exp [- 1.182 \times 10^5 \sigma^3 / (T (P_e - P_L)^2 \delta^2)] \quad (Z)$$

$$(\sigma - \sigma_1) a / kT = \ln (\phi_{1S} / \phi_1) + ((r - 1) / r) (\phi_{2S} - \phi_2) \quad (A)$$

$$\ln[(\phi_{2S} / \phi_2)^{1/r} / (\phi_{1S} / \phi_1)] = (\sigma_1 - \sigma_2) a / kT \quad (B)$$

Now, near $\phi_2 = 0$, Eq. (B) becomes

$$\phi_{2S} = \phi_2 \exp [r (\sigma_1 - \sigma_2) a / kT]$$

Putting in the numbers for polystyrene-cyclohexane, $\partial \phi_{2S} / \partial \phi_2 \approx 10^{-38}$ for $MW_2 = 2000$, $r = 13.4$, and even less for higher MW. The object here is to let $r = 1$ near $\phi_2 = 0$ and T near T_0 .

Thus $\phi_{2S} = \phi_2 \exp [(\sigma_1 - \sigma_2) a / kT]$ and so $(\partial \phi_{2S} / \partial \phi_2) = \exp [(\sigma_1 - \sigma_2) a / kT]$.

All of the details had to be included because it was only evident later that the surface tension term dominated. This had to be shown by direct calculation.

$$1. d = d_1 + (d_2 - d_1) \phi_{2S}$$

$$\partial d / \partial \phi_2 = (d_2 - d_1) (\partial \phi_{2S} / \partial \phi_2) = (d_2 - d_1) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

$$2. P_e = P_e(0) \phi_{1S} = P_e(0) (1 - \phi_{2S})$$

$$\partial P_e / \partial \phi_2 = - P_e(0) (\partial \phi_{2S} / \partial \phi_2) = - P_e(0) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

3. $B \approx 1 - 1/3 (1 - P_L/P_V)$ Here the approximation $P_e = P_V$ is used because this is a very small correction and they are close. Hence,

$$\partial B / \partial \phi_2 = (-1/3) (-1) \partial / \partial \phi_2 P_L/P_e$$

$$= (1/3) P_L \partial / \partial \phi_2 1/P_e \text{ and } = (1/3) P_L/P_e(0) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

$$4. \delta = 1 - d_G/d + 0.5 (d_G / d)^2 \text{ and } d_G = P_e MW_1/RT_1$$

$d_G/d = x$ is small so $\bar{\delta} \approx e^{-x}$

After some manipulation we have.

$$\partial\bar{\delta}/\partial\varphi_2 = \bar{\delta} [d_G/d + (d_G/d^2)(d_2 - d_1)] \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

Note ideal gas and T and φ_2 are orthogonal. These differentials don't vanish.

It was seen that the surface tension influence dominates wherever it occurs.

$\partial\varphi_{2S}/\partial\varphi_2 \approx$ only vanishes with r greater than 5, say.

To avoid clutter, the values for all these unknowns are left out and they are all in Jennings 2012.

International Journal of Thermodynamics article. This part is to establish the method.

Now, we get $\lim_{\varphi_2 \rightarrow 0} \partial\sigma/\partial\varphi_2 = (k T_0 / a) (1 - \exp [(\sigma_1 - \sigma_2) a / kT_0]) = (k T_0 / a) (0.9984)$.

This is arrived at by letting r = 1 in (A) above and partial differentiating with respect to φ_2 .

It is then seen that the surface tension terms dominate for all r, so $d\ln A/dK = 1/6K$.

σ_2 is significantly larger than σ_1 for this model system (polystyrene-cyclohexane).

Part 2

Getting all these quantities is the hard part and the rest is calculating

$\lim_{\varphi_2 \rightarrow 0} (\partial\ln A/\partial\varphi_2)/(\partial K/\partial\varphi_2) = 1/(6K)$, where A/K are the prefactor/exponent in (Z) above.

For r = 1, $1/(6K) = -0.002399$, or $K = -69.47$.

From the IAJER article by Jennings 2020, r = 13.4 and K = -64.56 for 10 solvents, polar & non-polar.

Deriving Jennings 2012 Equation (1) in the THEORY section there depends on $|1/(6K)|$ being small, so it is true for r = 1 to r = infinity. The surface tension dominates, as is noted by Blander and Katz 1975. The validity of $d\ln A/dK = 1/(6K)$ is therefore true for all r in the polystyrene-cyclohexane system and its integration constant for non-polar and polar solvents was calculated in Jennings' IAJER 2020 article. All of this puts Jennings' 2014 Polymers Research Journal equation on solid ground, which is formula (2), the equation for bubble nucleation in polymer solutions. The polymer solution data for this was first published by Jennings/Middleman 1985 MACROMOLECULES for polystyrene-cyclohexane.

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