A Scaling Approach for Understanding Bubble Nucleation in Polymer Foaming

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Understanding bubble nucleation is as necessary to polymer foaming as it is complex. So much is still to be determined that the problem seems daunting at times. However, by combining quality experimental results with incisive theoretical approaches, a greater understanding may be on the horizon. The problem is twofold: experimental nucleation rate data is limited and approximations must be made to classical nucleation theory due to the experimental inaccessibility of parameters. As such, the theory differs from experimental values by multiple orders of magnitude and predictions vary greatly based on approximations, making comparisons difficult.

We use a scaling approach to help bridge the gap. Using an optical viewing cell and high-speed camera, we have been able to determine nucleation rate data for a polystyrene/CO_2 system. The work to form a critical nucleus can then be extracted from this data and data from the literature. By comparing this work to that of CNT, it is possible to correlate a scaling equation that evaluates the inaccessible parameters by connecting nucleation theory to phase diagrams. We are extending this work further by developing a density functional theory approach that should provide a molecular-level understanding of the phase behavior of a polymer/CO_2 system.

CLASSICAL NUCLEATION THEORY

Nucleation describes the formation of a stable phase within another stable phase from a single supersaturated metastable phase. Specific to this paper, nucleation refers to the formation of gas bubbles from a metastable polymer/gas matrix.

Traditionally, nucleation has been described by the Classical Nucleation Theory (CNT) [1]. While this theory was originally developed for liquid droplet formation from a vapor, it can also be applied to the reverse case of interest here. The nucleation rate, J, is given by:

$$J = J_0 e^{-W/k_B T} \quad \textbf{(1)}$$

where W, k_B, and T represent the work required to form a critical nucleus, the Boltzmann factor, and the absolute temperature, respectively. J_0 is a kinetically-derived constant. Since W appears in the exponent, its accurate description has a larger impact on the nucleation rate than that of J_0. Gibbs derived the following formally rigorous equation for W:

$$W = \frac{16\pi\gamma^3}{3(\Delta P)^2} \quad \textbf{(2)}$$

where γ is the surface tension between the metastable polymer/gas mixture and the nucleating phase. ΔP is the difference between the pressure of the metastable phase (α) and the pressure of the nucleating phase if it were in the bulk with the same temperature and chemical potential as the metastable phase (β).

Unfortunately, it is currently not possible to experimentally measure the surface tension since it depends on the unobservable critical nucleus size. Therefore, in classical theory, the actual surface tension, γ, is approximated by the (bulk) planar interfacial tension, γ_∞, and the classical work is defined as:

$$W^{cl} = \frac{16\pi\left(\gamma_\infty\right)^3}{3\left(\Delta P\right)^2} \quad . \tag{3}$$

However, this approximation often leads to significant errors. It also violates thermodynamic considerations, as γ and thus W should vanish simultaneously at the mean-field spinodal, which cannot happen when the constant γ_∞ is used.

However, the issues raised result from experimental deficiencies, not from the theory itself, which is formally rigorous. To that end, quite a bit of work has gone into developing new theories that are statistical mechanically-rigorous, while also accurately describing both the interfacial and bulk properties, and utilizing equations of state (EOS) that accurately describe the metastable phase.

EXPERIMENTAL OBSERVATIONS OF NUCLEATION

While theoretical methods are important, they serve no purpose without experimental results. It should be noted that performing an experiment that truly results in homogeneous nucleation is extremely difficult. Preexisting gas cavities in the polymer matrix or on the walls of the container cannot be present, and minor impurities in the polymer can cause heterogeneous nucleation to take place. Even something as simple as nucleate boiling is not fully understood [2].

Nevertheless, quite a large number of nucleation experiments have been done. For the most part, they all do the same basic thing: they cause nucleation to take place, quench the sample to avoid coalescence, and then count the number of bubbles by one of various techniques. Assumptions are made with regard to the bubbles being spherical, not coalescing, and growing to detectable size.

As a slight aside, it should be noted for clarity that pressure drop rate, nucleation rate, and cell density can be considered equivalent. This has been experimentally verified by several groups using capillary nozzles [3, 4].

Experiments looking into nucleation behavior in polymer/CO_2 systems are quite rare at this point, but some experiments that have been performed on simpler systems by Strey can be informative [5]. The authors suggest that a nucleation-pulse method [6] that they used previously to study gas-liquid phase transitions can be adapted to study bubble nucleation. This method involves a binary gas-liquid mixture being supersaturated by a rapid pressure quench, which causes nucleation to take place. After a few milliseconds, the chamber is recompressed sufficiently to halt nucleation, yet still allow the bubbles that were formed to grow large enough to be detected. Constant angle Mie-scattering (CAMS) is used to detect the bubbles and allows the determination of their composition and size. Using this information and knowing the time between the quench and recompression, the nucleation rate can be determined. While this technique is useful, to our knowledge no further publications have been made on this subject.

While scarce, nucleation rate experiments for polymer/CO_2 systems have been performed by several groups. Ohshima's group has visually observed polymer foaming in batch and continuous processes using a high-speed camera attached to a microscope. For a variety of pressure drop rates, they can measure the cell number density as a function of time.

In batch foaming, micrographs were taken at different times which indicate nucleation and growth occurring simultaneously. Batch foaming results also indicate that nucleation rate is correlated to pressure drop rate. Their results indicate that continuous foaming may be influenced by flow and shear stresses and thus continuous and batch foaming may follow different mechanisms [7]. Very similar work was done several years ago by Park in conjunction with Ohshima, with a higher-speed camera and significantly larger pressure drop rates [8].

This method has recently been slightly modified and extended by our group in a batch process [9]. In this work, heterogeneous nucleation was more carefully mitigated by the use of a free-standing sample setup. This setup eliminates the sample contact with the viewing windows that was prevalent in the previous batch experiments. Further, this research looked at comparatively smaller pressure drop rates, which increases the range of pressure drop rates, and thus cell densities, that have been examined. This work also looked into the correlation of nucleation theory with phase diagrams using a scaling approach, which will be discussed in more detail in the next section.

SCALING APPROACH

As discussed previously, one of the major issues with applying CNT to polymer foaming is that the interfacial tension, γ, currently cannot be determined because the critical nucleus is not experimentally observable. Thus, the surface tension of the critical nucleus is replaced by that of a planar interface, γ_∞. The central idea of scaling approaches is to correlate the displacement between W and W^{cl} with the supersaturation by way of these two interfacial tensions.

This approach first begins by proposing that the work displacement, $W-W^{cl}$, is merely a function of temperature [10]. Scaling theories that are independent of material and uphold thermodynamic consistency (the vanishing of the barrier at the spinodal) have been previously proposed by several authors [11-13]. These theories correlate the relative work, W/W^{cl}, to the normalized supersaturation, $\xi=\Delta\mu/\Delta\mu_s=\Delta P/\Delta P_s$ (subscript s indicating a calculation at the spinodal). These quantities are determined from EOS calculations, which are tuned by adjusting their parameters to fit phase diagram information. Since phase diagrams are often experimentally available for polymer/CO_2 systems, this connection can be readily explored.

As mentioned previously, our group explored this approach for PS/CO_2 [14]. We compared the prediction accuracy of Sanchez-Lacombe (S-L EOS) and PC-SAFT EOS for solubility and phase diagram calculations for PS/CO_2. It was determined that PC-SAFT always provides a better prediction, though the difference is mitigated when an experimentally correlated binary interaction parameter is included.

For simplicity, S-L was used for the actual calculations. Knowing the conditions of the saturated initial state and the final state, the metastable state and corresponding hypothetical bulk phase (α and β, respectively) can be thermodynamically determined, thus garnering ΔP. At this point, W is only a function of γ, and thus (since J_0 is also only a function of γ), J_{ss} is only a function of γ. Given the experimental value for nucleation rate, the surface tension, γ, can be solved for. The planar surface tension, γ_∞, is then determinable from the literature. Once γ and γ_∞ are known, the relative work can be determined from the following equation:

$$\frac{W}{W^{cl}}=\left(\frac{\gamma}{\gamma_\infty}\right)^3 \qquad \textbf{(4)}$$

The EOS can also provide the chemical potentials whose ratio, $\xi = \Delta\mu/\Delta\mu_s$, is desired for scaling purposes. By plotting ξ versus W/W^{cl} and establishing thermodynamic boundary conditions, a scaling theory can be correlated. A graphical representation is shown below in Figure 1. The initial slope was also carefully calculated using diffuse interface theory. This work is the best result known for polymer/CO_2 systems, but more work is needed. Work on other polymer systems would be desirable, and, more importantly, it would be beneficial to examine this area with a more accurate EOS, such as SAFT.

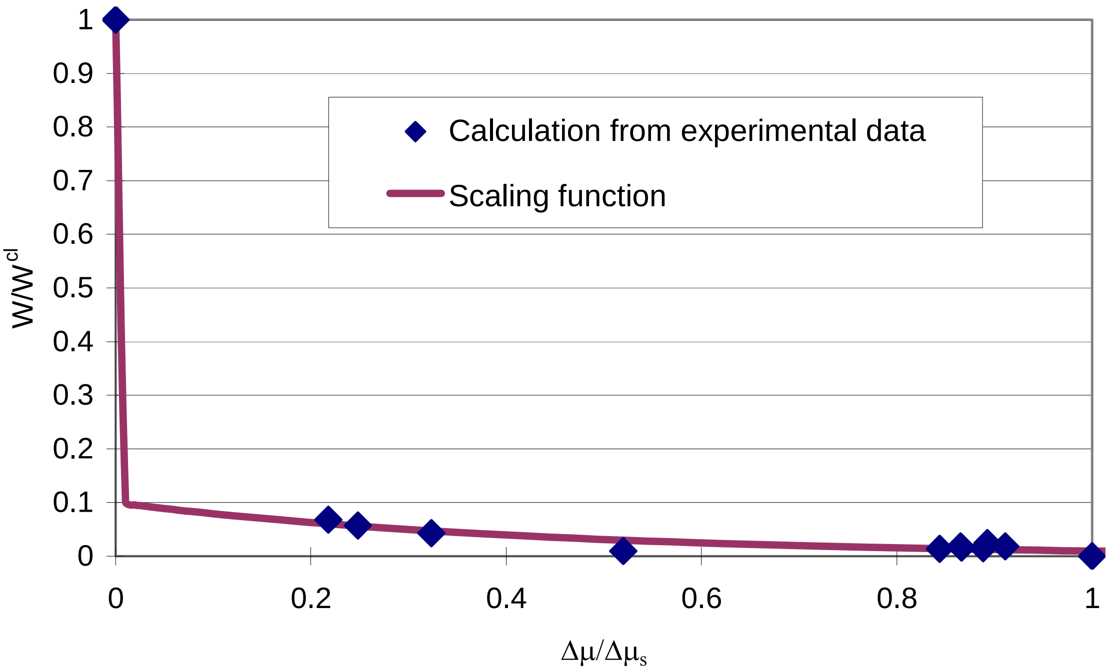

Figure 1: Calculation from Experimental Data and Prediction of the Scaling Function from Guo's Thesis.

SUMMARY

Some initial connections have been made between advanced computational approaches to bubble nucleation and the limited experimental data available. The scaling approach, while not quantitative, provides a framework to better understand the effect of process parameters on nucleation rates in polymer foaming.

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