Homogeneous Nucleation and the Spinodal Line

The limit of homogeneous nucleation in a liquid is shown to lie very close to its liquid spinodal line. It is also argued that the homogeneous nucleation prediction should be based on a comparison of the critical work of nucleation with the "potential well" energy instead of the kinetic molecular energy. The result is a new prediction of the liquid spinodal line for water that is valid to large negative pressures. This prediction compares well with spinodal points obtained by extrapolating liquid and vapor water data with the Himpan equation.

How Close to the Spinodal Line Can a Fluid Be Brought?

The minimum work required to bring a fluid from a homogeneous nucleation temperature, \( T_n \), to the spinodal temperature, \( T_s \), at the same pressure, \( p_n \), is given by the change of the thermodynamic availability between the two points, \( \Delta a \).

\[
\Delta a = (h_n - h_n) - T_n (s_n - s_n)
\]

(3)

where the reference, or dead state, is specified as the pressure, \( p_n \), and the initial temperature, \( T_n \). Figure 1 shows this hypothetical process. Notice that we arbitrarily consider an isobaric process. If there exists a path requiring less energy, then the calculation based on the isobaric model will be conservative.

Since the process from point (n) to point (s) is isobaric, equation (3) becomes

\[
\Delta a = J_{T_n}^T \left( c_p - \frac{T_n}{T} c_p \right) dT,
\]

(4)

and the problem of evaluating the minimum work reduces to that of specifying \( c_p(T) \) in the neighborhood of the spinodal line. We know from elementary thermodynamic considerations that

\[
\text{Limit of } \tau \rightarrow \tau_n c_p(T) = \text{finite} \quad \text{(5)}
\]

Among the functions that satisfy these conditions are: \( c_p(T) \sim (T_s - T)^{-b} \) where \( 1 > b > 0 \), and \( c_p \sim \ln(T_s - T) \). So too is any \( c_p \) that approaches infinity at \( T_s \) as a power weaker than a linear function of \((T - T_s)\).

We can clearly form an upper bound on \( \Delta a \) by factoring out the largest value of \((T - T_s)/T\). Thus

\[
\Delta a_{\text{upper bound}} = \Delta a = T_s - T_n \int_{T_n}^T c_p dT
\]

(6)

Substituting any one of the acceptable \( c_p \) functions in equation (6) we obtain

\[
\Delta a = D c_p(T_n) \frac{(T_s - T_n)^2}{T_s}
\]

(7)

where \( D \) is a number larger than unity. The value of \( D \) per molecule is then \( \Delta a / N_A \).

The conventional homogeneous nucleation theory says that nucleation is virtually sure to occur when the critical work required to trigger nucleation is on the order of magnitude of \( 10kT_n \) per nucleus.\(^3\)

\[ \frac{10kT_n}{N_n} < D c_p(T_n) \frac{(T_s - T_n)^2}{T_s} \]

(8)

where \( N_n \) is the number of liquid molecules in the region displaced by a nucleus bubble. Then

\[
\frac{(T_s - T_n)^2}{T_n T_s} > 10 RT \frac{1}{D c_p(T_n) N_n}
\]

(9)

\(^3\) The background for this assertion is developed in the next section.

---

1 This work was done while the first author was at the University of Kentucky.
2 This work was done under the support of the Electric Power Research Inst. (EPRI Contract RP 678-1) with Bimala Sehgal as project manager.
3 Contributed by the Heat Transfer Division for publication in the JOURNAL OF HEAT TRANSFER. Manuscript received by the Heat Transfer Division July 15, 1980.
where the molar ideal gas constant, \( R = k N_A \).

Consider next the order of magnitude of the three factors on the left side of equation (9): The term \( \frac{270}{N_A} \) approaches zero at the spinodal line, but we do not yet know how close \( T_n \) to \( T_s \) occurs. However, for water at 1 atm, \( R \) is 0.46 kJ/kg - K while \( c_p \) is 4.2 kJ/kg - K at saturation and at least 2.5 times this value at \( T_n \) (see, e.g., [3]). Thus for water, \( R/c_p < 0.04 \) and for other liquids it will be much less. Finally, Skripov [4] has calculated \( N_n \) for a variety of organic fluids at high pressure. He obtained numbers between 270 and 1010 at his observed nucleation temperatures. For water at 1 atm, \( N_n \) increases to 4000.

It follows that for water at 1 atm, \((T_n - T_s)/T_n\) is substantially less than 0.001 and for organic substances the result should be still less owing to far smaller values of \( R/c_p \). Then in general

\[
T_n - T_s \ll \sqrt{T_n/T_s} \approx T_n
\] (10)

If a comparable argument were developed for the vapor phase spinodal line, an equation similar to equation (9) would result. But in this case, \( N_n \) can be very small because there are very few vapor molecules within a volume equal to that occupied by a nucleus drop.

Equation (10) will therefore no longer be true. Nucleation thus occurs very close to the liquid spinodal, but we cannot expect it to occur anywhere near the vapor spinodal. This is exactly what we showed previously with experimental data in [1].

### On Locating the Spinodal

The conventional nucleation theory tells us that (see, e.g., [4]):

\[ j = \left[ \frac{\text{collisions}}{\text{relaxation time}} \right] \left[ \frac{s}{B \text{ collisions}} \right] \left[ \frac{1}{4\pi r_c^3 m^3} \right] \left[ \frac{m^3}{N_A \text{ molecules} \text{ pg} \text{ gm^{-1}}} \right] \]

This calculation and the experimental data of Skripov, et al. (see, e.g., [5]) can be interpreted to give somewhat varying results, but a good upper bound appears to be in the neighborhood of:

\[ j \approx (10)^{-8} \text{ or } G_b \approx 11.5 \] (14)

This corresponds with \( J \approx 10^{34} \text{ m}^{-3} \text{ s}^{-1} \).

The prediction of the spinodal line is then completed by substituting this value of \( j \) in equation (11), using Frenkel's expression [6]:

\[ \text{critical work} = 4\pi r_c^2 \text{ a/3} \] (15)

and a critical nucleus given by [4]

\[ r_c = 2a/[1 - V_f/V_g(\rho_{\text{sat}} - \rho_n)] \] (16)

Such predictions have frequently been offered in the past to predict homogeneous nucleation and they have worked fairly well at the spinodal temperatures that occur at positive pressures. These temperatures are usually in the range: 0.9 \( \approx T_n/T_s \) \( < 1.0 \) (see, e.g., [4]).

### A Modification of the Conventional Theory

Equations (11) and (12) are based on the concept that nucleation will occur as the critical work approaches the order of magnitude of the kinetic energy of molecules, characterized by \( kT \). We believe that the comparison should be made, not with the disturbance energy...
which can, in fact, vary enormously about the value of $kT$, but rather it should be compared with the fixed value of the energy required to separate one molecule from another.

This energy can best be characterized as the potential well energy, $\epsilon$ (see, e.g., [7]). This energy can be expressed in terms of the critical temperature as

$$\epsilon \approx 0.77 \frac{kT_c}{2}$$

(17)

Thus we propose to alter equations (12) and (11) to read

$$G_b = \frac{\text{critical work}}{kT_c} = 11.5$$

(18)

Figure 2 shows the resulting homogeneous-nucleation/spinodal line calculated from equations (11, 15) and (16), based on both equations (12) and (18). They are presented on pressure-temperature coordinates and the saturated liquid-vapor line is included for comparison. The two curves are nearly identical in the range of positive pressure because $T_c$ remains close to $T_{pc}$, but the curves diverge strongly at lower temperatures. We must next provide experimental evidence to show that the curve based on $\epsilon$ or $kT_c$ is superior to that based on $kT$.

The Approximate Location of the Spinodal Line by Extrapolation

The isotherms of a correct equation of state must match the known isotherms of water and steam in the stable regimes, it must satisfy equation (1), and it must define the two spinodal lines correctly. We seek an equation of state that is cubic in volume like the van der Waals equation, which can, in fact, vary enormously about the value of $kT$, but rather it should be compared with the fixed value of the energy required to separate one molecule from another.

We therefore used the Himpan cubic equation of state [8]

$$p = \frac{RT}{v - \beta} - \frac{\gamma}{(v - \alpha)(v - \delta)}$$

(19)

to fit the known facts. These facts consist of equation (1), the 1970 U.K. steam table vapor density and $(\partial p/\partial u)_{T=\text{sat}}$ data [9], and very precise liquid density data from Skripov's group [10-12] which extend into the superheated liquid regime. The Himpan equation has been proven to display the essential features of a correct equation of state and to give a good representation of real fluid data in the stable regimes. With four free constants it can provide a very close fit to any given isotherm.

We have used it to fit 38 different isotherms in the range $130^\circ C \leq T \leq 300^\circ C$ and $0.63 \leq \rho \leq 1.11$ bar. A modified Marquart subroutine for a nonlinear least squares [13] was used to evaluate $\alpha, \beta, \delta$, and $\gamma$ in each of the 38 cases. Each isotherm was then differentiated to locate the spinodal pressure in accordance with equation (3).

The resulting spinodal points are compared with the two homogeneous nucleation/spinodal line predictions. The points compare quite well with the prediction based on $j = 10^{-6}$ or $G_b = 11.5$ and the use of $kT_c$ in place of $kT$. There is increasing scatter in the extrapolation points as the temperature is reduced. This occurs because, as the temperature becomes less, minor discrepancies in the measured density at positive pressures are increasingly influential in the extrapolation.

Figure 3 shows a typical Himpan isotherm and the equation that defines it. The liquid data of Evstefeev [11] to which it is fitted in the liquid regime are included and the very high accuracy of the fit is given in the inset.

We therefore propose that, within a few degrees Celsius, the new homogeneous nucleation prediction can be used to specify $T_s$ at a given pressure. Our future program of research will be to use this equation to re-establish $\alpha, \beta, \delta$, and $\gamma$ for each isothermal equation. We can then use these resulting newly created data within the metastable regimes to rebuild the Keenan et al. fundamental equation [14] for water in such a way as to correctly account for the metastable regimes.

References


