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# Homogeneous Nucleation and the Spinodal Line<sup>2</sup>

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.

## Introduction

**Objective.** There have been some problems in the literature as to the relation between the homogeneous nucleation limit and the spinodal line. Indeed, when we [1] argued that the two were nearly the same in a superheated liquid, but quite different in a subcooled vapor, we were questioned sharply by referees. Some of them objected that the spinodal line was a fictional limit that could not ever be demonstrated experimentally.

At the time, our evidence that the two liquid limits were nearly the same was strong, but only circumstantial. A direct argument must still be offered to show that the two limits lie close to one another. Such a demonstration would have considerable value because the spinodal line—not the homogeneous limit—defines the local minimum in a correct equation of state. But only the latter can be established experimentally. If the two are close, then the spinodal line will be known as well. We would then have another constraint to add in the formulation of an equation of state that will have validity in the metastable liquid regime.

**The Spinodal Limit.** Conventional equations of state are written to describe the gas and liquid states as though they were continua—not made of molecules. Since such equations must satisfy the Maxwell-Gibbs requirement that

$$\int_{g_f}^{g_g} dg = \int_{\text{sat liquid}}^{\text{sat vapor}} v dp = 0 \quad (1)$$

we expect their isotherms to pass through ridges or "spines" of local maxima and minima defined by

$$\left. \frac{\partial p}{\partial v} \right|_T = 0 \quad (2)$$

Since the regions between these spines (or "spinodal lines" as they are called) is unstable, the state of real fluids cannot be brought all the way to either spinodal line. Molecular fluctuations will inevitably destabilize the fluid before the spine of instability is reached.

We subscribe to the view that the spinodal limit is nevertheless a physically useful concept in that the equation of state of a real fluid must satisfy both equations (1) and (2). Furthermore, we have previously shown [1, 2] that observations of homogeneous nucleation in liquids probably reach values quite close to the spinodal line. By providing an analytical demonstration that this is true, we will make it possible to specify the liquid spinodal in an equation of state for water. This is a key step in a program that we have undertaken (see [3]) to develop a fundamental equation that can be used in the metastable regimes.

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## 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,  $\Delta a$ .

$$\Delta a = (h_s - h_n) - T_n (s_s - s_n) \quad (3)$$

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

$$\Delta a = \int_{T_n}^{T_s} \left( c_p - \frac{T_n}{T} c_p \right) dT, \quad (4)$$

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

$$\text{Limit}_{T \rightarrow T_s} c_p(T) = \infty; \quad \text{Limit}_{T \rightarrow T_s} \left[ \int_T^{T_s} c_p dT \text{ and } \int_T^{T_s} \frac{c_p dT}{T} \right] = \text{finite} \quad (5)$$

Among the functions that satisfy these conditions are:  $c_p \sim (T_s - T)^{-b}$  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  $(T - T_n)/T$ . Thus

$$\Delta a_{\text{upper bound}} \equiv \Delta a_u = \frac{T_s - T_n}{T_s} \int_{T_n}^{T_s} c_p dT \quad (6)$$

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

$$\Delta a_u = D c_p(T_n) \frac{(T_s - T_n)^2}{T_s} \quad (7)$$

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

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.<sup>3</sup> It follows that

$$\frac{10kT_n}{N_n} < \frac{D c_p(T_n)}{N_A} \frac{(T_s - T_n)^2}{T_s} \quad (8)$$

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

$$\frac{(T_s - T_n)^2}{T_n T_s} > \frac{10}{D} \frac{R}{c_p(T_n) N_n} \quad (9)$$

<sup>3</sup> The background for this assertion is developed in the next section.

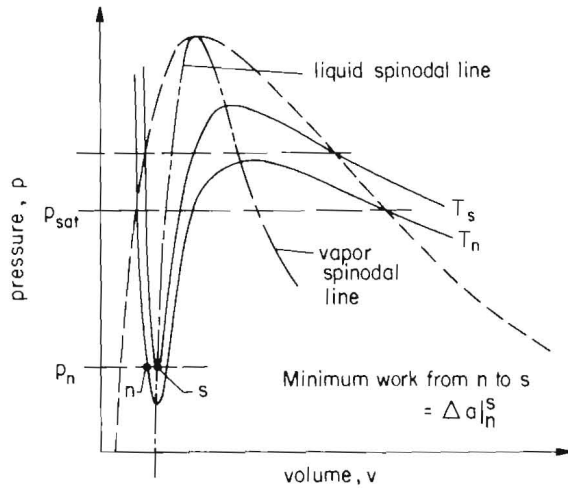


Fig. 1 Process of triggering nucleation from the point of homogeneous nucleation,  $n$ , to the point,  $s$ , on the spinodal line at the same pressure

where the molar ideal gas constant,  $R \equiv kN_A$ .

Consider next the order of magnitude of the three factors on the left side of equation (9): The term  $(10/D) < 10$ .  $R/c_p$  clearly approaches zero at the spinodal line, but we do not yet know how close  $T_n$  is to  $T_s$ . 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,  $(T_s - T_n)/T_n$  is substantially less than 0.01 and for organic substances the result should be still less owing to far smaller values of  $R/c_p$ . Then in general

$$T_s - T_n \ll \sqrt{T_n T_s} \simeq T_n \quad (10)$$

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]):

$$j \frac{\text{nucleation events}}{\text{molecule-collision}} = \frac{J \frac{\text{Nucleation events}}{\text{m}^3 \text{s}}}{N \frac{\text{molecules}}{\text{m}^3} B \frac{\text{collisions}}{\text{s}}} = e^{-Gb} \quad (11)$$

where the Gibbs number,  $G_b$ , is

$$G_b = \frac{\text{critical work to trigger nucleation}}{kT} \quad (12)$$

The value of  $j$  at which nucleation absolutely must occur is the largest possible one. It corresponds with the minimum possible value of the critical work.

One way of specifying the maximum possible value of  $j$  is to imagine that just one nucleation event occurs every relaxation-time within the population of liquid displaced by the nucleus bubble of radius,  $r_c$ . Thus,

$$j = \left[ \frac{\text{collisions}}{\text{relaxation time}} \right] \left[ \frac{s}{B \text{ collisions}} \right] \left[ \frac{1}{\frac{4}{3} \pi r_c^3 m^3} \right] \times \left[ \frac{M}{N_A} \frac{gm}{\text{molecules}} \frac{m^3}{\rho_f gm} \right] \quad (13)$$

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:

$$j \simeq (10)^{-5} \text{ or } G_b \simeq 11.5 \quad (14)$$

This corresponds with  $J \simeq 10^{34} \text{ m}^{-3} \text{ s}^{-1}$ .

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

$$\text{critical work} = 4\pi r_c^2 \sigma / 3 \quad (15)$$

and a critical nucleus given by [4]

$$r_c = 2\sigma / [(1 - v_f/v_g)(p_{\text{sat}} - p_n)] \quad (16)$$

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:  $0.9 \geq T_s/T_c < 1.0$  (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

### Nomenclature

$a$  = isobaric, thermodynamic availability function,  $h - (T_{\text{dead state}})s$   
 $B$  = rate of molecular interactions or "collisions"  
 $b$  = exponent of  $(T_s - T)$  in a specific heat formula  
 $c_p$  = molar specific heat at constant pressure  
 $D$  = a number on the order of unity  
 $G_b$  = the Gibbs number, critical work/characteristic energy of the fluid  
 $g$  = the Gibbs free energy,  $h - Ts$   
 $h$  = molar enthalpy  
 $J$  = volumetric rate of nucleation events  
 $j$  = rate of nucleation events per molecular

interaction  
 $k$  = Boltzmann's constant  
 $M$  = molecular weight  
 $N$  = molecules per unit volume at nucleation  
 $N_A$  = Avogadro's number  
 $p$  = pressure  
 $R$  = ideal gas constant  
 $r_c$  = critical radius of an unstable nucleus  
 $s$  = molar entropy  
 $T$  = temperature  
 $v$  = molar specific volume  
 $\alpha, \beta, \delta, \gamma$  = constants in the Himpan equation of state (19)

$\Delta a, \Delta a_u$  = change in availability from ( $n$ ) to ( $s$ ). Upper bound on  $\Delta a$   
 $\rho$  = density,  $1/v$

### Subscripts

$c$  = a property at the thermodynamic critical point (except as it appears in  $r_c$ )  
 $f, g$  = the saturation liquid and vapor states  
 $n$  = a property at the point of homogeneous nucleation  
 $s$  = a property on a spinodal line  
 $\text{sat}$  = a property that is saturated at  $T = T_n$

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

$$\epsilon \approx 0.77 kT_c \quad (17)$$

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

$$Gb = \frac{\text{critical work}}{kT_c} = 11.5 \quad (18)$$

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  $T_s$  remains close to  $T_c$ , 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, and which can be fitted to these facts, all of which are known except perhaps the location of the spinodal line. We cannot use the van der Waals equation for this purpose because it has no free constants and it is only exactly true for a fluid with a critical compressibility equal to  $\frac{3}{8}$ .

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

$$p = \frac{RT}{v - \beta} - \frac{\gamma}{(v - \alpha)(v - \delta)} \quad (19)$$

to fit the known facts. These facts consist of equation (1), the 1970 U.K. steam table vapor density and  $(\partial p / \partial v)_{T_{\text{sat}}}$  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  $130^\circ\text{C} \leq T \leq 300^\circ\text{C}$  and  $0.63 \leq p \leq 111$  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 (2).

The resulting spinodal points are compared with the two homogeneous nucleation/spinodal line predictions. The points compare quite well with the prediction based on  $j = 10^{-5}$  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.

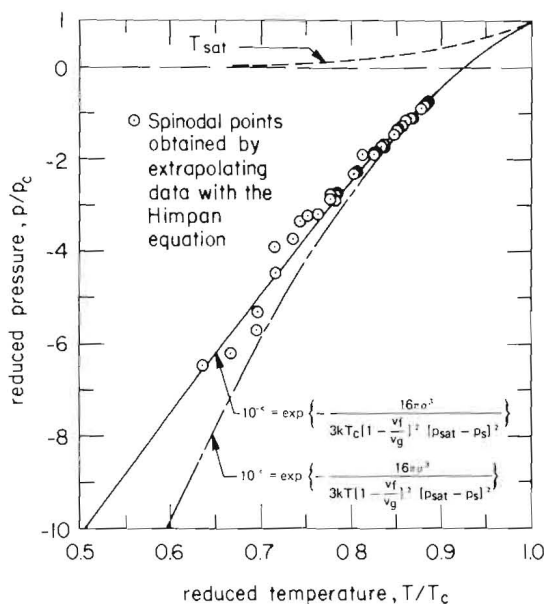


Fig. 2 Comparison of the present prediction with the conventional prediction and with data extrapolations

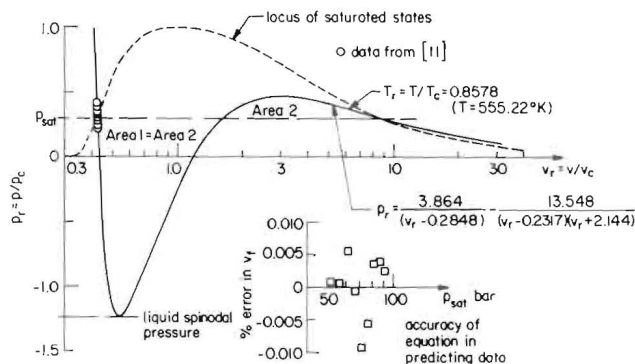


Fig. 3 A typical Himpan equation isotherm

### Conclusions

- 1 The difference between the highest possible liquid homogeneous nucleation temperature and the liquid spinodal temperature at the same pressure is negligible in comparison with the spinodal temperature. Therefore we can use the homogeneous nucleation temperature as a close approximation to the spinodal temperature.
- 2 The first conclusion does not apply in the metastable vapor regime.
- 3 The appropriate energy to use in the denominator of  $G_b$  appears to be  $kT_c$  instead of  $kT$ .
- 4 The spinodal line for liquid water is given to good accuracy by

$$10^{-5} = \exp \left[ - \frac{16\pi\sigma^3}{3kT_c \left[ 1 - \frac{v_l}{v_g} \right]^2 (p_{\text{sat}} - p_s)^2} \right] \quad (20)$$

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