

## A Reexamination of Homogeneous Nucleation Theory

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### ABSTRACT

The homogeneous nucleation theory of liquid droplets in supersaturated vapors is reviewed. Taking into consideration the *microscopic surface tension* and extrapolating from the triple point to the critical point ( $T = T_c$ ) of the liquid-gas phase transition, we reexamine homogeneous nucleation theory. A calculation of the growth rate for microscopic clusters due to the incorporation of much smaller clusters (instead of single molecules) is given and an appropriate variable, *scaled supersaturation*, is presented to study the mechanism of homogeneous nucleation. For a given nucleation rate, the scaled supersaturation is expected to be nearly independent of temperature below  $T_c$ ; this is confirmed by experimental data. A generalized form for the droplet model is proposed. Previous theories ("classical," Lothe-Pound, Reiss, Katz, Cohen) are shown to be special cases of this generalized form and all are shown to be invalid near the critical point. A quantitative theory is made by extrapolating Fisher's droplet model from the critical region to the triple point. For the free energy of embryo formation we include the contributions due to internal vibrations and self-avoiding walks. The microscopic surface tension for the droplet is estimated from the measured coexistence curve; it is found to agree with the bulk macroscopic surface tension near the triple and critical points and to be smaller in the intermediate region. With these considerations we have calculated the scaled supersaturation for water vapor as a function of temperature for given measured nucleation rates. The proposed theory is in good agreement with experiment.

### 1. Introduction

Homogeneous nucleation for liquid droplets in supersaturated vapors has been studied both for the thermodynamic properties of metastable states (Feder *et al.*, 1966) and for droplet formation phenomena in the expanding flows encountered in the atmosphere, in wind tunnels, in rocket exhausts, etc. It has also been used both as a basic theoretical foundation for heterogeneous nucleation [where we either take into account such suitable modifications as the effects of contact angle and particle size (Fletcher, 1962), or simply introduce into the free energy of an embryo the excess binding energy of the foreign particle over that of the homogeneous molecule which it replaces (Allen and Kassner, 1969)] and for the homogeneous nucleation of a solid from a fluid where the relevant surface tensions are not known (Fletcher, 1962).

The classical theory of homogeneous nucleation was developed by Volmer, Becker and Doering and Zeldovich [the references are given in the review of Feder *et al.* (1966), Fletcher (1962), and Byers (1965)]. Two basic assumptions were used: 1) it is an equilibrium rate theory (the principle of detailed balance and the stationary state model), and 2) the equilibrium concentration of clusters is obtained by assuming that the

free energy of a cluster is equal to the bulk free energy plus the free energy due to the cluster surface.

This classical theory has been accepted as correct on the basis of its good agreement with the results of existing measurements (Feder *et al.*, 1966; Katz and Ostermeyer, 1967; Katz, 1970). Additional contributions to the free energy of embryo formation due to the translation and rotation of the droplet were considered by Frenkel (1946) and Kuhrt (1952). However, the first quantitative result with these considerations was presented by Lothe and Pound (1962). Their calculations increased the nucleation rate by  $10^{17}$  as compared to that of the classical theory. In order to restore agreement between their theory and available experiments, Feder *et al.* (1966) suggested that either the surface tension for small droplets needed to be increased some 15% above that for bulk liquid, or that the pre-exponential factor in the nucleation rate needed to be decreased by some  $10^{-15}$ . This "translation-rotation paradox" has generated a great controversy. Reiss *et al.* (1968) have criticized this idea and have presented a model which assumed that the free energy of a droplet with fixed boundaries and a center of mass which fluctuates over the entire droplet is equal to the free energy of that same number of molecules in the bulk liquid plus a surface free energy without corrections due to translation and rotation. Their calculation for the nucleation rate decreases the pre-exponential factor of Lothe and Pound by some  $10^{-10}$ – $10^{-12}$  (this variation is due to

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the actual fluctuation of the center of mass) with the same macroscopic bulk liquid surface tension. With the same basic physical picture as Reiss *et al.*, but a slightly different physical argument and by considering the droplet as a liquid drop instead of a cluster, Reiss (1970) has recently restored the agreement with classical theory to within 0.01% by using a different treatment of the partition function. Furthermore, Katz (1970) has recently reexamined the experimental data for different substances with more accurate and careful measurements using diffusion chamber techniques. His data have shown good agreement with the classical theory. Experimentally, at least, it seems likely that the classical theory is acceptable.

However, it has been shown (Kirkwood and Buff, 1949; Tolman, 1949) that the surface tension of small droplets should be less than the surface tension of bulk liquid. Instead of the macroscopic surface tension measured in bulk experiments one should use a "microscopic" tension, valid for a droplet containing  $10^2$ – $10^4$  molecules. From the classical theory, a few percent change in the surface tension will affect the nucleation rate significantly. Thus, without further justification for using the macroscopic surface tension data for small droplets, the classical theory still has serious shortcoming and is far from complete.

It is also noticed that the previous theories for studying homogeneous nucleation are restricted to low temperatures far below the critical temperature  $T_c$  of the liquid-gas phase transition. In order to establish a correct theory for the study of homogeneous nucleation, it is necessary to check the validity of the theory for an extensive temperature range that includes the critical region. We have recently presented a calculation of the nucleation rate near the critical temperature (Eggington *et al.*, 1971), combining the standard nucleation rate formula and Fisher's droplet picture (Fisher, 1967a, b). At a constant "scaled supersaturation" [see Section 6; also Eggington *et al.* (1971) and Sarkies and Frankel (1971)] we have found a strong critical slowing down for the nucleation rate.

In this paper we attempt to reexamine homogeneous nucleation theory because of three problems:

- 1) The correction term to the free energy of the classical theory.
- 2) The question of the microscopic vs the bulk surface tension.
- 3) The critical behavior.

Therefore, we develop a quantitative theory by extrapolating Fisher's droplet model from the critical region to low temperatures down to the triple point.

In Section 2, the standard formula for the calculation of the nucleation rate with equilibrium rate theory is reviewed. Near the critical point we calculate the growth rate for the microscopic clusters due to the incorporation of much smaller clusters (instead of single molecules)

with size  $l_k$  ["coherence effect"; see Eggington *et al.* (1971)].

A generalized form originally proposed by Fisher (1967a) is introduced in Section 3 to study the theory of homogeneous nucleation for both the low temperature and the critical regions. Previous theories, including the classical theory (e.g., Byers, 1965), the Lothe-Pound theory (1962), the Reiss-Katz-Cohen theory (1968), and a recent theory by Reiss (1970) are classified as special cases of this generalized form. It is found that these theories are invalid in the critical region.

In Section 4 we present the nucleation rate for Fisher's droplet model. The idea of "scaling laws" (Kadanoff, 1966), a useful tool in the critical region, is adapted to introduce the scaled supersaturation in order to have a better understanding of the mechanism for homogeneous nucleation theory. We have found that for a given nucleation rate this scaled supersaturation is almost independent of the temperature at low temperatures [cf. Byers (1965), Table 3.3] and has a logarithmic singularity at the critical point.

A quantitative theory is presented in Section 4. We extrapolate Fisher's droplet model from the critical region to low temperatures. For the free energy of embryo formation we include the influence of the self-avoiding walks suggested by Fisher (1966) and add the contributions due to the internal vibrations (sound waves within a droplet and surface waves on its surface). With the proposed quantitative theory, the microscopic surface tension for the droplet is estimated for various substances by the shape to the coexistence curve obtained from experimental measurements (density on the vapor pressure curve). Our microscopic surface tension agrees with the (macroscopic) bulk surface tension near the critical and triple points; it is smaller in between. With the proposed model, a quantitative calculation of the nucleation rate is presented; the agreement with available experimental data is good for water.

In the conclusion (Section 5) further experiments are proposed.

## 2. Droplet growth and nucleation rate

We shall now re-derive the usual expressions for the growth of very small droplets and the nucleation rate in a supersaturated vapor. A minor modification results from a "coherence" effect, important perhaps very near  $T_c$ .

Imagine a fixed number of gas particles in a fixed volume. First, pressure and temperature are chosen such that the gas is on the coexistence curve (vapor pressure curve) but no liquid is in the vessel. Then pressure or temperature are suddenly changed such that the vapor is supersaturated (metastable). Now we want to know how quickly the vapor condenses into the newly formed liquid state, and what is the mechanism for this process.

To solve this problem quantitatively, nucleation theory assumes that even in a non-supersaturated vapor there are always tiny liquid droplets present as thermodynamic fluctuations of finite lifetime. [It is well known (Kadanoff *et al.*, 1967) that at least in the critical region there exist strong analogies between fluids and magnets; in this case, for a ferromagnet below the Curie point, not all spins are in one direction at a given instant of time: some are reversed.] If the vapor is supersaturated, then the number of small droplets growing to larger sizes exceeds the number of clusters shrinking (evaporating) to smaller sizes. Thus, more and more larger droplets are formed which finally build up a visible fog of liquid droplets; condensation has occurred.

The concentration  $n'_l(t)$  of  $l$  droplets (i.e., droplets containing  $l$  molecules) can grow and shrink with time  $t$  by four different processes:

- 1) A smaller droplet grows to size  $l$  by incorporation of other molecules.
- 2) A larger droplet shrinks to size  $l$  by evaporation.
- 3) The  $l$  droplet loses molecules by evaporation.
- 4) The  $l$  droplet incorporates molecules.

Now it is usually *assumed* that the droplets grow and shrink only by incorporation and evaporation of single molecules. We prefer the more general assumption that they grow and shrink predominantly in steps of  $l_\xi$  molecules instead of one molecule. Here  $l_\xi$  is an integer and is probably large near the critical point of the fluid (Eggington *et al.*, 1971). The usual assumption corresponds to the special case  $l_\xi=1$  and is probably justified far below  $T_c$ . Thus, if  $b_\xi$  is the rate at which  $l_\xi$  droplets are incorporated into an  $l$  droplet (assumed to be independent of  $l$ ) and  $\alpha_l$  the rate at which they evaporate from an  $l$  droplet (per unit time and area), and if  $S_l$  is the average area of a (not necessarily spherical)  $l$  droplet, then the change of the concentrations  $n'_l$  with time is given by the following four-term equation:

$$\frac{dn'_l(t)}{dt} = n'_{l-l_\xi} b_\xi S_{l-l_\xi} + n'_{l+l_\xi} \alpha_{l+l_\xi} S_{l+l_\xi} - n'_l (\alpha_l S_l + b_\xi S_l). \quad (2.1)$$

If the concentrations do not change with time, then the corresponding equilibrium distribution  $n_l$  will be determined by the Helmholtz free energy  $f_l$  of the droplets (with the assumption that droplet-droplet interactions are negligible); thus, we have

$$n_l \propto \exp[-(f_l - \mu l)]. \quad (2.2)$$

For this equilibrium distribution we know that

$$n_l \alpha_l S_l = n_{l-l_\xi} b_\xi S_{l-l_\xi}, \quad (2.3)$$

because the number of  $l$  droplets newly formed in equilibrium from  $(l-l_\xi)$  droplets then equals the num-

ber of  $l$  droplets becoming  $(l-l_\xi)$  droplets by evaporation. Eliminating  $\alpha_l$  from (2.3) we find from (2.1) that

$$(b_\xi S_{l_\xi})^{-1} \frac{dc_l(t)}{dt} = c_{l+l_\xi} - c_l - g_l (c_l - c_{l-l_\xi}), \quad (2.4a)$$

with

$$c_l(t) = n'_l(t)/n_l, \quad (2.4b)$$

and

$$g_l = S_{l-l_\xi} n_{l-l_\xi} / S n_l. \quad (2.4c)$$

Fig. 1 shows an IBM 1130 computer solution of (2.4). Initially ( $t=0$ ),  $n'_l$  is the equilibrium concentration (2.2) on the coexistence curve and  $n_l$  is the equilibrium concentration (2.2) for the metastable (supersaturated) vapor. In the latter case the chemical potential is higher than on the coexistence curve. The curves show first that the concentrations for all droplet sizes except the smallest one are growing. Then for several small droplet sizes the concentrations begin to fall, while the number of larger droplets still increases. Finally, at the latest time shown in the figure, all concentrations are decreasing. This simply means that many small droplets are incorporated into others to form larger droplets. The final solution would be one single liquid droplet containing all available molecules. (We neglect the fact that the supersaturation is diminished because more and more molecules are in the liquid state. Thus, only the initial stages of the condensation process are described correctly; at a later time the condensation by droplet growth might be stopped because the vapor is no longer supersaturated.)

If  $l \gg l_\xi$  we can, to a good approximation, replace the differences in (2.4a) by differentials; e.g.,  $c_{l+l_\xi} - c_l = l_\xi \partial c_l / \partial l$ . Then after multiplication with  $n_l$  (2.4a) becomes

$$\frac{\partial n'_l}{\partial t} = b_\xi l_\xi^2 \frac{\partial}{\partial l} \left( S n_l \frac{\partial c_l}{\partial l} \right). \quad (2.5)$$

By defining a current

$$J_l = -b_\xi l_\xi^2 S n_l \frac{\partial c_l}{\partial l}, \quad (2.6a)$$

Eq. (2.5) gives us the continuity equation

$$\partial n'_l / \partial t + \partial J_l / \partial l = 0. \quad (2.6b)$$

If we assume that there is a constant flow of  $l_\xi$  droplets into the vessel to keep  $n_{l_\xi}$  constant in time, and that all droplets reaching a size  $l=L$  ( $L$  very large) are removed from the system, then after some time all  $n'_l$  will remain constant; this means a stationary state has been reached. Then  $J_l$  will be independent of  $l$  according to (2.6b) and thus equal to the incoming flow of  $l_\xi$  droplets and to the number of macroscopic  $L$  droplets formed (and removed) per unit time. This  $J_l$

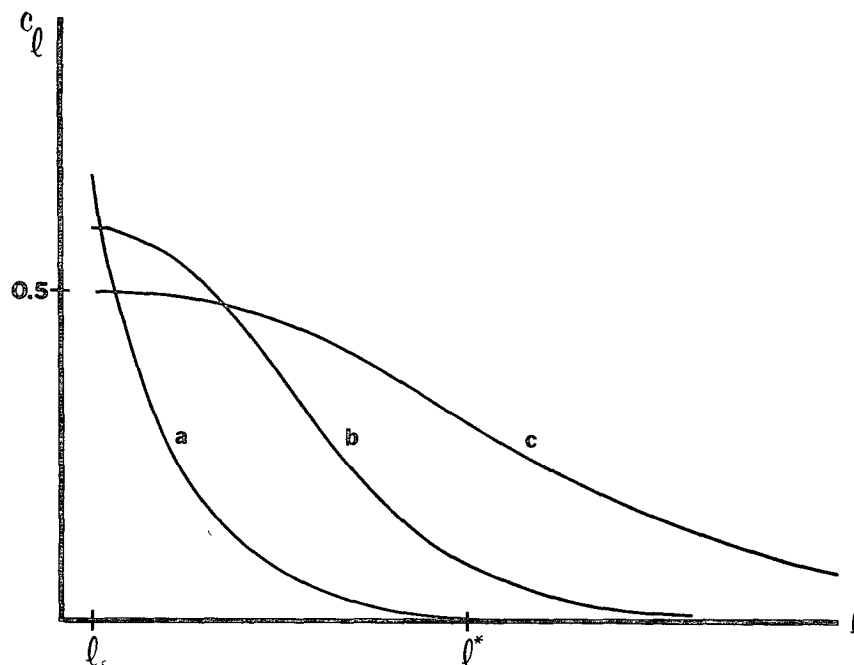


FIG. 1. Growth of relative droplet concentrations,  $c_l = n'_l/n_l$ , with time  $t$  as a function of the droplet size  $l$ : curve  $a$ ,  $t=0$ ; curve  $b$ ,  $t=3/(b_l S_{li})$ ; curve  $c$ ,  $t=102/(b_l S_{li})$ . [ $n_l$  is given by (2.2) and (3.6);  $n'_l$  is the actual concentration;  $A=0.4$  with the definition (4.3a);  $l_c$  and  $l$  are defined by (3.7) and (4.4), respectively]. For  $\text{CO}_2$  at  $T=T_c-8K$ ,  $1/(b_l S_{li})=0.3 \times 10^{-7}$  sec. For  $A=0.2$  the time lag is larger (varying as  $A^{-2}$ ) and  $c_{l_c}$  is closer to 1 (cf. Feder *et al.*, 1966, p. 120).

is then called the nucleation rate and is the rate at which large liquid droplets are formed from the super-saturated vapor. We integrate (2.6a) with respect to  $l$  to obtain

$$\int_{l_c}^L J/(b_l l_c^2 S_{mi}) dl = -c_l |_{l_c}^L = 1$$

because  $c_{l_c}=1$ ,  $c_L=0$ . Thus,

$$J = b_l l_c^2 \int_0^\infty (S_{mi})^{-1} dl. \quad (2.7)$$

This is the basic equation of nucleation theory. [A factor  $l_c$  was erroneously omitted by Eggington *et al.* (1971)]. If we include the fact, taken into account by Katz *et al.* (1966), that droplets grow by droplets of various size  $i$ , then our factor  $b_l l_c^2$  in (2.7) is replaced by  $\sum_i b(i) i^2 [\approx 10 b_l l_c^3 \propto l_c^{0.3}$ , using  $b(i) = P_i (2\pi m i k T)^{-1}$ ], (3.6) and (3.7). In our droplet model the strong thermodynamic decrease of the nucleation rate observed by Katz *et al.* (1966) does not occur. We equate the incorporation rate with the impinging rate (sticking coefficient = 1), although it might be smaller by two orders of magnitude (Okuyama and Zung, 1967). As we will see later,  $S_{mi}$  has a minimum at  $l=l^* \gg 1$ , and only values of  $l$  about  $l^*$  are important in the integral (2.7). Therefore, the integration runs from 0 to  $\infty$ . (Typical values for  $l_c$  and  $l^*$  near  $T_c$  are  $10^2$  and  $10^6$ , respectively; they are smaller at low temperatures.) By integrating

from  $l$  to  $\infty$  we find the concentrations  $n'_l = n_l c_l$  in this hypothetical stationary state from:

$$c_l = \int_l^\infty S_i^{-1} n_i^{-1} dl / \int_0^\infty S_i^{-1} n_i^{-1} dl. \quad (2.8)$$

In the stationary state with a time-independent non-zero current  $J$ , the relative concentration  $c_l$  is 1 for small  $l$  and  $\frac{1}{2}$  for  $l=l^*$ . The above equations are derived from this hypothetical steady state with a constant flow of  $l_c$  droplets into the vessel. From our more realistic calculation leading to Fig. 1 we see that this assumption is not exact but a good approximation for the small supersaturations we are interested in. (An error of a factor of 2 is not important for our theory.) A more detailed study, assuming  $c_l$  to be constant, has been given by Abraham (1969).

Our calculation of the droplet growth process is analogous to the one given by Feder *et al.* (1966), but differs by the  $l_c$  factors. The nucleation rate (2.7) alone can be derived without using the droplet growth equation (2.4) [Byers (1965); Eggington *et al.* (1971)].

Thus, we have reexamined and generalized one basic assumption of homogeneous nucleation theory, the equilibrium rate theory (2.7). The generalization is that the  $l_c$  factors are important very near  $T_c$ . Fig. 1 shows that the stationary-state assumption, by which the nucleation rate (2.7) is calculated, is a sufficient approximation.

### 3. Droplet model

We now outline a quantitative model to calculate the equilibrium concentrations  $n_l$  given by (2.2).

It is generally known that the second basic assumption for homogeneous nucleation theory is introduced by assuming that the free energy  $f_l$ , which determines the cluster equilibrium distribution (2.2), contains the bulk free energy plus the surface free energy of the cluster. However, many additional contributions due to different physical arguments for the free energy of embryo formation have been considered. Here, we simply summarize different theories as follows:

- 1) Classical theory (cf. Byers, 1965; Fletcher, 1962)

*Assumption:*

The free energy  $f_l$  of  $l$  clusters can be expressed as:

$$f_{l,c} = lE + \gamma S_l, \quad S_l = S_l l^{\frac{2}{3}}, \quad (3.1)$$

where  $E$  is the microscopic bulk free energy,  $\gamma$  the surface tension, and  $S_l$  the surface area for an  $l$  cluster.

- 2) Lothe-Pound theory (1962).

*Assumption:*

The  $l$  cluster can be treated as a large molecule; thus, its free energy contains contributions due to the translation and rotation of the whole cluster. In this case we have

$$f_{l,L-P} = lE + \gamma S_l - kT \ln \left( \frac{l^{\frac{3}{2}}}{\lambda^3} \right) - kT \ln \left( \frac{4.76 v_B l^{\frac{3}{2}}}{\lambda^3} \right), \quad (3.2)$$

where  $\lambda = h(2\pi mkT)^{-\frac{1}{2}}$  is the thermal de Broglie wavelength, 4.76 results from the geometric factors of a spherical droplet, and  $v_B$  is the molecular volume. The third term is the translational contribution, the fourth the rotational.

- 3) Reiss-Katz-Cohen theory (1968).

*Assumption:*

A droplet with fixed boundaries is considered, its center of mass fluctuating over the entire droplet (without considering the droplet rotation and translation). The actual fluctuation of the center of mass is calculated. The different limits for the fluctuation give

$$f_{l,RKC_1} = lE + \gamma S_l - \frac{3}{2} kT \ln l + \text{constant}_1, \quad (3.3a)$$

$$f_{l,RKC_2} = lE + \gamma S_l - \frac{1}{2} kT \ln l + \text{constant}_2, \quad (3.3b)$$

- 4) Reiss theory (1970).

*Assumption:*

The droplet is considered as a liquid drop instead of a cluster; the partition function can thus be written as

$$f_{l,R} = lE + \gamma S_l - \text{constant}/l^{\frac{1}{3}}. \quad (3.4)$$

It is easily noticed that all theories listed above can be expressed in a general form as

$$f_l = lE + \gamma S_l l^{\sigma} + \tau kT \ln l + \text{constant}, \quad (3.5)$$

where  $\tau kT \ln l$  and the constant term can be considered as the corrections for the free energy of an  $l$  cluster due to different physical arguments, and  $\sigma$  is a parameter allowing different geometric shapes of the cluster ( $0 < \sigma < 1$ ; since the above theories involve spherical droplets,  $\sigma = \frac{2}{3}$ ). On the coexistence (vapor pressure) curve the chemical potential equals  $E$ .

This free energy form was originally proposed by Fisher (1967b) to study the critical phenomena of a liquid-gas phase transition. With the assumption that the excluded volume effect between clusters is negligible, the equation of state for the infinite system is a generalization of the ideal gas result,  $P/(kT) = n_1$ , to a mixture of ideal gases, the components being the subset of all 1 clusters, all 2 clusters, all 3 droplets, etc. [using  $n_l$  from (2.2)]. Thus, the pressure is

$$P/kT = \sum_{l=1}^{\infty} n_l = q_0 \sum_{l=1}^{\infty} l^{-\tau} x^{(l\sigma)} y^l \quad (3.6a)$$

where

$$\left. \begin{aligned} kT \ln x &= -S_1 \gamma (\propto T - T_c \text{ near } T_c) \\ kT \ln y &= \mu - \mu_c \end{aligned} \right\}, \quad (3.6b)$$

where  $x=y=1$  at the critical point. In Eqs. (3.6)  $T_c$  is the critical temperature,  $\mu_c$  the chemical potential on the coexistence curve, and  $q_0$  comes from the constant term appearing in  $f_l$ . Notice that near  $T_c$  the microscopic surface tension  $\gamma$  is a linear function of  $T - T_c$ , in contrast to the bulk surface tension which is generally proportional to  $(T_c - T)^{1.3}$ . This linearity assumption will prevent the higher thermodynamic derivatives with respect to temperature (specific heat) from having a singularity at  $T = T_c$  and  $\rho \neq \rho_c$ . (It is known that the specific heat is finite in a one-phase region.) With Fisher's droplet model the parameters  $\tau$  and  $\sigma$  can be determined by directly measurable critical indices [e.g., along the critical isotherm:  $(\rho_c - \rho) \propto (\mu_c - \mu)^{\tau-2} = (\mu_c - \mu)^{1/\delta}$  for  $T = T_c$ ; along the coexistence curve:  $(\rho_c - \rho) \propto (T_c - T)^{(\tau-2)/\sigma} = (T_c - T)^{\beta}$ ]. The so-called "scaling laws" (Kadanoff *et al.*, 1967) are satisfied by this droplet model (Fisher, 1967a). The critical exponent  $\delta$  for water (Straub, 1970) is found experimentally to be 4.3, giving a value of  $\tau = 2.233$ ; similarly,  $\beta$  has been found to be 0.35, resulting in a value of  $\sigma = \frac{2}{3}$ . The comparison of Fisher's droplet model with experiment near  $T_c$  gives good agreement (Kiang and Stauffer, 1970); here the microscopic surface tension is determined by the shape of the coexistence curve (cf. Appendix B). In the sum (3.6a) the important contributions for the static critical properties come from  $l \sim l_c$ , where

$$l_c = |\ln x|^{-1/\sigma}. \quad (3.7)$$

The diameter of the  $l_\xi$  droplets can be interpreted as a coherence length diverging at the critical point (Stauffer *et al.*, 1971a,b).

From the previous discussion, Fisher's droplet model also gives a general form for the theories of homogeneous nucleation far below  $T_c$ . Therefore, it is proposed that Fisher's droplet picture be considered as a good candidate to study homogeneous nucleation theory for the temperature region from the triple point to the critical point. On the other hand, the previous theories discussed give  $-4 \leq \tau \leq 0$  (values much smaller than the experimental result of 2.23) and do not give the correct critical indices. These theories will also predict infinite pressure and density at the critical point. [cf. (3.6)]. Therefore, they cannot be extrapolated to the critical region.

To extrapolate Fisher's droplet picture to the low temperature region, we propose a quantitative theory. For the free energy of embryo formation we include the contributions due to internal vibrations and self-avoiding walks. We follow Reiss (1970) in neglecting rotational and translational contributions. We calculate the contributions due to internal sound and surface waves (Appendix A); they give a logarithmic contribution to  $f_l$  because their wavelengths are restricted in the finite droplet. The calculation of self-avoiding walks was presented by Fisher (1966). In combining these contributions, we find  $\tau \approx 2.2$  in good agreement with the experimental result.

The other exponent  $\sigma$  is determined near  $T_c$  by the critical indices. (For spherical droplets  $\sigma = \frac{2}{3}$ , but the droplets need not be spherical.) Since  $\sigma$  is the parameter connected with the geometric shape, we assume it to hold also for low temperatures. Hence, a quantitative droplet model is introduced to study homogeneous nucleation theory for the temperature region from the triple point to the critical point.

Stillinger (1967, and private communication) proposed a different droplet model which agrees with scaling assumptions slightly below and at  $T_c$  and does not employ a microscopic surface tension. His theory contains many free parameters and has not been checked by experiments. His droplet concentrations behave differently for  $l \ll l_\xi$  and  $l \gg l_\xi$ . While Stillinger's derivation of this result does not seem convincing (see Appendix A), it would not be implausible for microdroplets to behave differently from macroscopic droplets, the size boundary just being  $l_\xi$ . [K. Binder (unpublished) found a similar transition by Monte Carlo calculations.] Thus, we might multiply our result for  $n_l$  by a function  $F(l/l_\xi)$  with  $F(0) = 1$ . If for large  $z$ ,  $F(z)$  is proportional to a  $z$  power of order unity, as in Stillinger's theory, then our later results for the nucleation rate and the scaled supersaturation do not change drastically.

We conclude, as the most important difference from previous theories, that this droplet model is applicable

not only to the nucleation rate but also to static properties. Thus, we can use a microscopic surface tension, estimated from the density on the vapor pressure curve.

#### 4. Quantitative calculations

We shall now give a formula for the nucleation rate and compare its predictions with low temperature experiments.

With the equilibrium rate theory (2.7) and the proposed droplet model (3.6) the nucleation rate can be written as (Eggington *et al.*, 1971)

$$J_s = b_\xi S_\xi l_\xi^{-\tau+3} |\ln x|^{(\tau+1-\sigma)/\sigma} A^{\tau+1-\sigma} \times \left[ \sum_{n=0}^{\infty} A^{-n\sigma} \Gamma(n\sigma + \tau - 1 + \sigma) / n! \right]^{-1}, \quad (4.1)$$

which, for water, may be written as

$$J_s \approx 3.4 b_\xi S_\xi l_\xi^{-0.7} |\ln x|^{3.85} A^{6.7} \exp(-0.148 A^{-2}), \quad (4.2)$$

where  $A$ , the scaled supersaturation, is defined as

$$A = \ln y / |\ln x|^{1/\sigma}. \quad (4.3a)$$

[Note (Fletcher, 1962) that  $\ln y = (\mu - \mu_c) / kT$  in an ideal gas is equal to  $\ln S = \ln(P/P_\infty)$ , where  $S$  is the supersaturation ratio,  $P_\infty$  the vapor pressure,  $\Gamma$  the Gamma function and  $\ln x$  the microscopic surface tension, as defined in Section 3 (see Appendix B).] Since  $\ln S$  is very small in the critical region, we have  $(P - P_\infty) / P_\infty = (\rho_c k T_c / P_c) (\mu - \mu_c) / kT$ ; thus

$$\ln S = A |\ln x|^{1/\sigma} \quad (\text{low temperature}), \quad (4.3b)$$

$$\ln S = 3.5 A |\ln x|^{1/\sigma} \quad (\text{critical region}). \quad (4.3c)$$

Eq. (4.1) is derived exactly from (2.7) and (3.6), whereas (4.2) is the standard approximation for the nucleation rate (Byers, 1965) valid for small  $A$  and obtained from the fact that the quantity  $n_l S_l$  in (2.7) has a minimum as a function of  $l$  at  $l = l^*$  with

$$l^* / l_\xi = (1.5 A)^{-3}, \quad A \ll 1. \quad (4.4)$$

##### a. Scaled supersaturation

We note that (4.1) has a form similar to the scaling homogeneity assumption used for the equation of state near the critical point (Widom, 1965; Kadanoff *et al.*, 1967). The nucleation rate is proportional to  $|\ln x|^{(\tau+1-\sigma)/\sigma}$ , and is a homogeneous function of  $\ln y$  (supersaturation) and  $|\ln x|^{1/\sigma}$  (surface tension). Utilizing the "scaling laws" (Kadanoff *et al.*, 1967), we introduce  $A$ , as defined before, as a proper quantity to describe the *metastability* of the liquid-gas transition.

From (4.2), we observe that the nucleation rate depends exponentially on the scaled supersaturation  $A$  and is proportional to a finite power of  $\ln x$  (surface tension). Therefore, for a given nucleation rate, we expect the scaled supersaturation  $A$  to be roughly in-

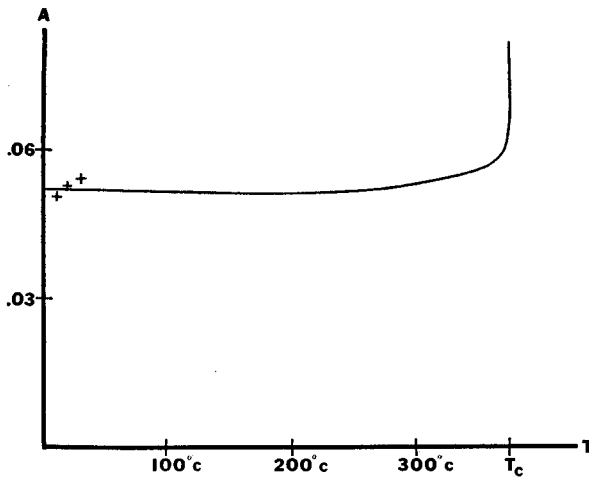


FIG. 2. Expected scaled supersaturation  $A$  in water vapor as a function of temperature for a nucleation rate  $J=1 \text{ cm}^{-3} \text{ sec}^{-1}$  as calculated from (4.1) and (4.2) with  $h_t=1$ . For low temperatures  $A=0.051$  is nearly temperature independent. A 2% increase in  $A$  enlarges  $J$  by a factor of 10, i.e.,  $A=0.0565$  for  $J=10^5$ . The experimental data (crosses) are those of Katz and Ostermier (1967) for water scaled by the microscopic surface tension [Eq. (B.4)]. If we fit  $A$  on the measured supersaturation (at  $J=1 \text{ cm}^{-3} \text{ sec}^{-1}$  and  $240\text{K} < T < 290\text{K}$ ) using (4.3b) with the bulk surface tension instead of the microscopic [Eq. (B.3)], we find temperature-independent values for water ( $A=0.051$ ), nonane ( $A=0.050$ ), octane ( $A=0.049$ ), heptane ( $A=0.048$ ) and hexane ( $A=0.0465$ ).

dependent of the temperature for the low temperature region and to have a logarithmic singularity at the critical point. If  $A$  is kept constant, then the nucleation rate as a function of temperature vanishes as  $(T_c - T)^{(\tau+1-\sigma)/\sigma}$ . The numerical calculation of the nucleation rate for  $\text{CO}_2$  near  $T_c$  was presented by Eggington *et al.* (1971). For  $\ln x = -0.1$ ,  $A=0.045$  at  $J=10^5$ , and  $A=0.09$  at  $J=10^{15}$ .

To verify the idea of scaled supersaturation we examine the experimental data of Katz and Ostermier (1967) and Katz (1970) for different substances [similar results are given in Table 3.3 of Byers (1965)]. In Katz's data, the nucleation rate is fixed at unity and the supersaturation curve is given as a function of temperature. By using a macroscopic bulk liquid surface tension and his measured data of supersaturation  $S$  and temperature  $T$ , we have calculated the scaled supersaturation  $A$  as a function of  $T/T_c$  for different substances; results are in the legend to Fig. 2. There are two interesting results: 1) for a given  $J$ , the scaled supersaturation is roughly independent of the temperature as expected, and 2) the scaled supersaturation  $A$  for different substances has the same value (around 0.05) for the given nucleation rate  $J=1 \text{ cm}^{-3} \text{ sec}^{-1}$ .

The physical significance of the scaled supersaturation is that it can be simply interpreted as a proper quantity to measure the metastability. For the metastable state, we consider not only the supersaturation but also the surface tension. In other words, the com-

petition between the bulk energy and surface energy is the basic mechanism for the metastable state. At the coexistence curve,  $A=0$ ; at the spinodal line (Chu *et al.*, 1969), we expect  $A=O(1)$ ; and for a visible fog,  $A \gtrsim 0.04$ .

### b. Microscopic surface tension

From our proposed droplet model the microscopic surface tension can be estimated by the shape of the experimentally determined coexistence curve measured by experiments (see Appendix B). The microscopic surface tension is calculated from the triple point to the critical point for water. We have found that: 1) near the triple point and very near the critical point, the microscopic surface tension is in agreement with the bulk surface tension, and that 2) in the intermediate region, the microscopic surface tension is smaller than that of the bulk surface tension.

Hence, from our calculations, we have found a justification for using the bulk surface tension in the low temperature region, as used by the previous theories.

With the calculated microscopic surface tension, we once again use the experimental data for water from Katz and Ostermier (1967) and plot  $A$  vs  $T/T_c$  for nucleation rate  $J=1$ . Three such points are shown in Fig. 2. Therefore, with the correct microscopic surface tension, the scaled supersaturation is expected to be nearly temperature-independent for low temperatures.

Actually, it is more convenient to determine the scaled supersaturation by the dimensionless quantity  $(T/T_c) \ln x$  (which simply comes from  $\rho/\rho_c$  on the coexistence curve) than by the surface tension itself, since fewer parameters are involved. The microscopic surface tension for water vapor is plotted in Fig. 3, the temperature ranging from near the triple point to near the critical point.

### c. Comparison of experimental and theoretical nucleation rates

For fixed nucleation rate  $J$  we have used a computer program based on (4.1) to calculate the scaled supersaturation  $A$  for water vapor as a function of  $T/T_c$ . The result, shown in Fig. 2, is in good agreement with experiments for low temperatures (Katz and Ostermier, 1967), the experiments being regarded as accurate to within 15%. We strongly suggest further experiments in the critical and the intermediate regions and more accurate measurements at low temperatures to check our theory.

In a recent theory, Sarkies and Frankel (1971) have also discussed a quantity near the critical region analogous to what we have called the scaled supersaturation. If scaling laws are valid, they found that this quantity remains constant as  $T \rightarrow T_c$ , whereas our  $A$  diverges logarithmically because of the critical slowing down (vanishing of the pre-exponential factor).

## 5. Conclusions and discussion

As a result of the present work in which homogeneous nucleation theory is reexamined and extended to the critical region, it is concluded that the proposed droplet model agrees with experimental results. The shortcomings of the previous homogeneous nucleation theories are resolved by: 1) determining the microscopic surface tension (Fig. 3), 2) evaluating contributions to the droplet free energy due to internal vibrations and self-avoiding walks (Appendix A), and 3) choosing a droplet model which is valid in the critical as well as the low temperature region.

The concept of a scaled supersaturation is introduced as a proper description of metastability and nucleation. Since the temperature dependence of  $q_0$  in (3.6) cannot be determined from the droplet model, it is neglected in (B.3). However, it does influence the microscopic surface tension and the scaled supersaturation. Except near  $T_c$ , this problem might weakly influence our quantitative predictions for the nucleation rate from  $\ln x$ . Our theoretical prediction for  $A$  in heptane<sup>3</sup> at  $J=10^5 \text{ cm}^{-3} \text{ sec}^{-1}$  might be about one-half the value measured by Katz (1970). Thus, this question deserves further study.

As we have mentioned, the macroscopic surface tension data can be used in the low temperature region.

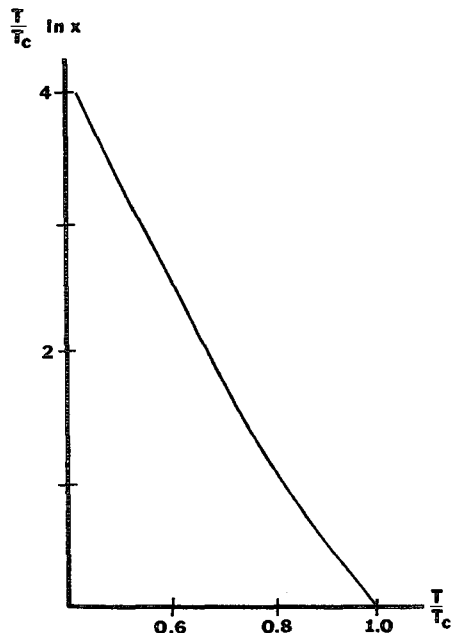


FIG. 3. Temperature variation of  $(T/T_c) \ln x$  for water, calculated from (B.3). This quantity is essentially the microscopic surface tension per molecule, measured in units of  $kT_c$  [Eq. (B.5)]. The values for hexane, heptane and octane are roughly the same; they are higher by 20% for  $C_2H_5OH$  and are lower by 20% for HCl and by 50% for the quantum gas  $H_2$ .

<sup>3</sup> The critical indices  $\tau$  and  $\sigma$  in the hydrocarbons are not known to us. The nucleation rate, however, depends crucially on their numerical values.

In order to verify our theory, we have proposed and are carrying out homogeneous nucleation experiments in the intermediate and critical region (see Eggington *et al.*, 1971); the results will be presented in a future publication. We also hope to report later on applications to cloud physics, heterogeneous nucleation, and fluid-solid homogeneous nucleation.

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## APPENDIX A

### Logarithmic Free Energy Contributions from Internal Vibrations

Here we estimate the contributions of surface waves and internal sound waves to the logarithmic term  $kT \ln l$  in the free energy of an  $l$  droplet. Stillinger (1967) made a similar calculation but did not estimate the sound wave contributions. Abraham and Canosa (1969) calculated the one-dimensional sound wave contribution in agreement with (A2). We will add to our result the logarithmic term calculated by Fisher (1966) from random walk considerations, and we will find the desired result,  $\tau=2.2$ .

We start from the formula for the free energy of a system of uncoupled harmonic oscillators having the (undamped) eigenfrequencies  $\omega_i$ ,  $i=1, 2, \dots, n$ :

$$F = kT \sum_{i=1}^n \ln[1 - \exp(-h\omega_i/kT)] \\ \approx kT \sum_{i=1}^n \ln(h\omega_i/kT), \quad (\text{A1})$$

where  $h=2\pi\hbar$  is Planck's constant, and we assume  $h\omega_i \ll kT$ . We identify the internal vibrations of a droplet (bulk compressional waves and surface capillary waves) with these harmonic oscillators. Eq. (A1) holds if the frequencies are temperature-independent. It seems justified to us to assume, for the small wavelengths occurring within the droplet, that the wave motions are adiabatic and not isothermal. Then we expect the vibration frequencies to be roughly temperature-independent even at the critical point, where the surface tension (and in general the bulk sound velocity as well) vanishes. In this respect our calculation differs from Stillinger's; thus, in contrast to his result our contribution to the logarithmic term is the same at  $T_c$  and slightly below  $T_c$ . Thus, we feel it is a good approximation to apply (A1) to the internal vibrations of a droplet.

A simple one-dimensional example (see Stillinger, 1967) shows how a  $\ln l$  term can arise from (A1). We assume  $\omega_i \propto i/n$ . Then from Stirling's formula  $[n!$



$= (n/e)^n (2\pi n)^{\frac{1}{2}}$  we find for large  $n$  that:

$$\begin{aligned} f(n) &= F/kT = \sum_i \ln(i/n) + n \cdot \text{constant} \\ &= \ln(n!/n^n) + n \cdot \text{constant} = \ln(2\pi n)^{\frac{1}{2}} + n \cdot \text{constant}' \\ &= \left(\frac{1}{2}\right) \ln n + n \cdot \text{constant}'' \\ &\quad + \text{a constant and smaller terms.} \quad (\text{A2}) \end{aligned}$$

For the general calculation in  $d$  dimensions we assume that  $f(n) = F/kT$  has the form

$$f(n) = an + b \ln n + \text{constant} + \dots$$

Then for large  $n$  we have

$$f(2n) - 2f(n) = -b \ln n + \text{constant}. \quad (\text{A3})$$

First we repeat the one-dimensional calculation using (A3) and  $\hbar\omega_i/kT = \epsilon i/n$ ,  $\epsilon \ll 1$ . As a result we have

$$\begin{aligned} f(2n) - 2f(n) &= \sum_{i=1}^{2n} \ln\left(\frac{\epsilon i}{2n}\right) - 2 \sum_{i=1}^n \ln\left(\frac{\epsilon i}{n}\right) \\ &= \sum_{i=1}^n \left\{ \ln\frac{\epsilon i}{n} + \ln\left[\frac{\epsilon(i-\frac{1}{2})}{n}\right] - 2 \ln\frac{\epsilon i}{n} \right\} \\ &= \sum_{i=1}^n \ln\left(\frac{i-\frac{1}{2}}{i}\right) \approx \sum_{i=1}^n \left(-\frac{1}{2i}\right) = -\frac{1}{2} \ln n + \text{constant}, \end{aligned}$$

in agreement with the exact result from Stirling's formula. For the same calculation in  $d$  dimensions, we assume that the frequencies are proportional to (wavevector) $^g$ , such that

$$\hbar\omega_i^{(n)}/(kT) = \epsilon(i/n)^{g/d}, \quad (\text{A4})$$

where  $n$  gives the total number of degrees of freedom for this type of excitation. For example, in three dimensions the number  $i$  of wavevectors smaller than some maximum  $k_i$  is proportional to  $k_i$ . Thus,  $\omega_i \propto k_i \propto i^{\frac{1}{3}}$  in agreement with (A4). Eq. (A4) is chosen such that the number of wavevectors smaller than some  $K$  is proportional to  $K^d$ , as it should be. Then

$$\begin{aligned} f(2n) - f(n) &= \sum_{i=1}^n \{ \ln[\omega_{2i}^{(2n)}/\omega_i^{(n)}] + \ln[\omega_{2i-1}^{(2n)}/\omega_i^{(n)}] \} \\ &= \frac{g}{d} \sum_{i=1}^n \ln\left(\frac{i-\frac{1}{2}}{i}\right) \approx \frac{-g}{2d} \sum_{i=1}^n \frac{1}{i} = -\frac{g}{2d} \ln n + \dots \quad (\text{A5}) \end{aligned}$$

Thus, the vibrations contribute to the droplet free energy the term

$$kT(g/2d) \ln(n), \quad n \gg 1, \quad (\text{A6})$$

apart from the leading term (proportional to  $n$ ) and constant terms. For  $d > 1$  this disagrees with Abraham

and Canosa (1969). In this derivation the logarithm arises from  $\sum 1/i$ ; thus, our result does not change if we omit a fixed number of small  $i$  [because (A4) is invalid for small  $i$ ] or a fixed fraction of large  $i$  (because  $\hbar\omega_i$  is no longer much smaller than  $kT$  for large  $i$ ).

The numbers  $n_{\text{bulk}}$  and  $n_{\text{surf}}$ , for sound waves and surface waves, respectively, are determined by the number of molecules in the bulk volume and in the surface. Assuming (see Stauffer *et al.*, 1971a) that  $n_{\text{surf}} \propto (n_{\text{bulk}})^{\frac{2}{3}} \propto l^3$  for an  $l$  droplet in three dimensions, we find the following logarithmic contributions from bulk and surface waves:

$$\text{Bulk: } \frac{1}{6} kT \ln(l) \quad \text{for } g=1, d=3, \quad (\text{A7a})$$

$$\text{Surface: } \frac{1}{4} \times \frac{3}{2} \cdot kT \ln(n_{\text{surf}}) = \frac{1}{4} kT \ln l \\ \text{for } g=\frac{3}{2}, d=2. \quad (\text{A7b})$$

According to Fisher (1966), for a three-dimensional lattice gas, random walk considerations give an entropy resulting in a free energy contribution of  $(1.75 \pm 0.05)kT \ln l$ . Adding these three contributions we find a term  $(2.17 \pm 0.05)kT \ln l$  for the droplet free energy. Fisher's droplet model near  $T_c$  (Section 3) requires the numerical factor  $\tau$  to be  $2 + 1/\delta = 2.19 \pm 0.01$  in the three-dimensional lattice gas. We find the agreement to be surprisingly good, although it could well be fortuitous. One might argue, for example, that the translational and rotational degrees of freedom for the droplet give a contribution of  $-4kT(\ln l)$  [Kuhrt, 1952] or that the surface wave contribution is already included in the random walk result,  $1.75kT(\ln l)$ . However, both arguments do not seem to be reliable. The most recent theories give no logarithmic contributions from rotations and translations (Reiss, 1970, Kikuchi, 1971). In addition, the lattice gas model used for the random walk considerations gives no time-dependent properties and therefore does not correctly describe the surface waves. On the other hand, there might be other contributions to the logarithmic term which are overlooked in our phenomenological approach. Thus, we conclude that the parameter  $\tau$  can be determined by experiment at  $T = T_c$ . We give a possible explanation for its value around 2.2; if this explanation is correct, then  $\tau$  is temperature-independent.

It should be mentioned that higher order corrections in the droplet free energy expansion are not excluded by our calculation. In fact, we argued the next term to be  $bkTl^{g-1}$  (Stauffer *et al.*, 1971b). If  $b \ll 1$  this term is not important for the nucleation theory. (A comparison of the resulting equation of state with experiment is in preparation.)

## APPENDIX B

### Microscopic Surface Tension

This appendix gives the formula which allows one to measure the microscopic surface tension for the

droplet free energy. The exponents  $\sigma$  and  $\tau$  are assumed to be 0.667 and 2.23, respectively, at all temperatures.

The particle density in the droplet model [Eq. (3.6)] is given by

$$\rho = \frac{\partial P}{\partial \mu} = q_0 \sum_{l=1}^{\infty} l^{1-\tau} x^{(l^\sigma)} y^l, \quad (\text{B1})$$

where  $x < 1$  below  $T_c$ . On the coexistence curve,  $y = 1$ , while on the critical isotherm,  $T = T_c$  and  $x = 1$ . Thus,  $x = y = 1$  at the critical point, and the critical density  $\rho_c$  is given therefore by  $\rho_c = q_0 \zeta (\tau - 1)$ ,  $\zeta$  being the Zeta function (see Kiang, 1970). Replacing the sum by an integral, as is appropriate near  $T_c$ , we find on the coexistence curve near  $T_c$ , with  $\ln x = (1/D)(T - T_c)/T_c$ , that

$$(\rho_c - \rho)/\rho_c = 1.2 |\ln x|^\beta = 1.2 D^{-\beta} \left( \frac{T_c - T}{T_c} \right)^\beta, \quad (\text{B2})$$

where  $\beta = (\tau - 2)/\sigma$ . The density  $\rho$  on the coexistence curve can be measured and  $D$  can then be determined from (B.2); in general,  $D$  lies between 0.25 and 0.7. Thus,  $-\ln x = (1, \dots, 4)(T_c - T)/T_c$  near  $T_c$ .

Instead of simply extrapolating this result [i.e., Eq. (A2)] to low temperatures near the triple point we use (A1). If we take into account only the first term of this series expansion in powers of  $y \propto e^{\mu/kT}$ , we find the ideal gas behavior: only single molecules, no larger clusters occur, and  $P = n_1 kT$  from (3.6). These ideal gas results are known to be correct for a vapor near the triple point; in this case we have

$$\rho = q_0 x; \quad \rho/\rho_c = x / \left[ \zeta \left( 1 + \frac{1}{\delta} \right) \right] = x/5. \quad (\text{B3})$$

In the region intermediate between the ideal gas region and the critical region we need to evaluate more than one term in (A1). These terms are of the form

$$x = 5\rho/\rho_c - \sum_{l=2}^{\infty} l^{-1.233} x^{l^{2/3}}. \quad (\text{B4})$$

Thus, we can determine  $x$  from (B2) near  $T_c$ , using (B3) at low temperatures and (B4) in the intermediate region.

According to Section 3,  $\ln x$  determines the microscopic surface tension  $\gamma_m$  by

$$\gamma_m = -kT(\ln x)/S_1, \quad (\text{B5})$$

where  $S_l = S_1 l^\sigma$  is the surface area of an  $l$  droplet. Thus, the microscopic surface tension is determined from the density on the coexistence curve. Our results for water vapor are plotted in Fig. 3 (Landolt-Boernstein, 1960). With  $S_1 = 0.45 \times 10^{-14}$  cm<sup>2</sup> for water, we find from (B5) a microscopic surface tension of 80 dyn cm<sup>-1</sup> at 0C, as compared with 75 dyn cm<sup>-1</sup> for the bulk surface

tension (Katz, 1970). Because our assumption for  $S_1$  is hardly very accurate and we neglected the temperature dependence of  $q_0$  in (B3), we can conclude that both surface tensions agree within the accuracy of our theory at the triple point. But at 0C the microscopic surface tension decreases more strongly with increasing temperature than the bulk surface tension.

A better method, which requires very accurate data, was proposed by Tseng *et al.* (1940) and Abraham (1968). They evaluate  $\ln x$  (called  $w$  in their works) from the compressibility factor  $P/\rho kT = (\sum l^{-\tau} x^l) / (\sum l^{-\tau} x^{l^\sigma})$ . Then the temperature dependence of  $q_0$  cancels out. Their values of  $\ln x$  in water are larger than ours by 4.4 at low temperatures because they used  $\tau = -\frac{3}{2}$ . With our  $\tau = 2.2$  we find  $\ln x$  from the compressibility factor to be 10% larger than in Fig. 3 for water at 0C;  $q_0$  seems to be roughly temperature-independent. This method cannot be used closer to  $T_c$  because  $P_c/(\rho_c kT_c)$  in the droplet model is too large for water (Kiang, 1970; Straub, 1970).

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