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Classical Nucleation Theory with a Tolman Correction

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The effect of the Tolman correction for the surface tension of small droplets on the classical Becker–Doering theory of nucleation is studied near the critical temperature T_c. Also a generalization of the kinetic prefactor is studied together with this correction. No qualitative change in the very small slope of the curve of the reduced supercooling as a function of $(1 - T)/T_c$ at constant nucleation rates was found.

KEY WORDS: Nucleation; droplets; surface tension; Tolman correction.

1. INTRODUCTION

Anomalously large supercoolings near the critical point were observed by various workers for CO_2,(1) IW,(2) and LW(3) as they compared their results with the classical nucleation theory of Becker and Doering. It is now believed that the origin of this is a critical slowing down of the growth of droplets of radius greater than the critical radius.(4) Experiments, e.g., LW,(3) were done by visual observation and droplets therefore escape detection until their radii are much larger than the critical radius. Consequently one may fail to observe nucleation. "A test of nucleation theory near the critical point must therefore be left to the future" as Goldburg(5) put it.

Tolman(6) in 1949 and more recently Nonnenmacher(7) and Vogelsberg(8) studied the effect of the droplet size on the surface tension. These works suggest that the surface tension σ should be replaced by

$$\sigma \rightarrow \sigma\left(1 + \frac{\delta}{r}\right)^{-1}$$

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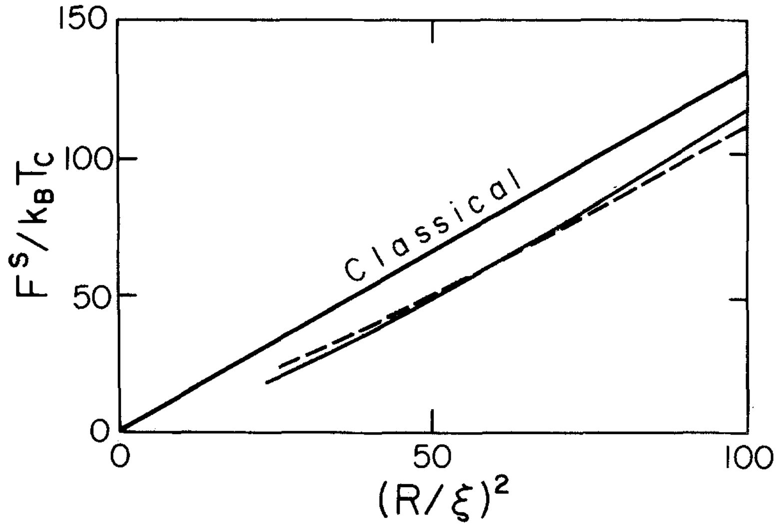


Fig. 1. Surface free energy F^s/k_BT_c plotted vs. $(R/\xi)^2$ as obtained by Furukawa and Binder.[15] Broken curve is the Tolman corrected surface free energy.

where δ is the Tolman parameter. Tolman reported positive values for δ for water in the temperature range 10–50° C of about 1Å. Figure 1 shows a fit with δ equal to the correlation length of the Tolman corrected surface free energy on Monte Carlo data of the three-dimensional lattice gas model by Furukawa and Binder.[15] Indication that δ can be negative was found by Franke[9] based on Monte Carlo simulations of the surface tension of the two-dimensional square lattice percolation clusters.

We will include the Tolman correction for the surface tension in the classical Becker–Doering theory of nucleation, as well as in a generalized form of this theory and study its influence on the reduced supercooling near T_c. It is hoped that future experiments to determine the true nucleation rate by Goldburg and collaborators[10] as well as Monte Carlo studies of the nucleation rate in the three-dimensional Ising model[11] will make it possible to determine quantitatively the phenomenological parameter entering the Tolman formula.

2. THE CRITICAL RADIUS AND THE NUCLEATION BARRIER

In the classical Becker–Doering theory of homogeneous nucleation the free energy for formation of a spherical droplet is given by

$$\Delta F_{\text{cl}} = 4\pi r^2\sigma - \tfrac{4}{3}\pi r^3 \Delta\rho\delta\mu \tag{2.1}$$

$\delta\mu$ being the difference in the chemical potential between the supersaturated vapor and the two-phase equilibrium state at the given average density, and $\Delta\rho$ the difference between the equilibrium densities corresponding to the liquid and vapor. ΔF_{cl} has a maximum at

$$r_{cl}^* = \frac{2\sigma}{\Delta\rho\delta\mu} \tag{2.2}$$

the critical radius and the height of the nucleation barrier is

$$(\Delta F_{cl})^* = \frac{16}{3}\frac{\pi\sigma^3}{(\Delta\rho\delta\mu)^2} \tag{2.3}$$

Replacing σ by $\sigma(1+\delta/r)^{-1}$ in Eq. (2.1) we get

$$\Delta F = 4\pi r^2\sigma(1+\delta/r)^{-1} - \tfrac{4}{3}\pi r^3\Delta\rho\delta\mu \tag{2.4}$$

The critical radius for ΔF is now found to be

$$r^* = \frac{\sigma + [(\delta\Delta\rho\delta\mu + \sigma)\sigma]^{1/2}}{\Delta\rho\delta\mu} - \delta \tag{2.5}$$

Define

$$y = \frac{\delta\Delta\rho\delta\mu}{\sigma} \tag{2.6}$$

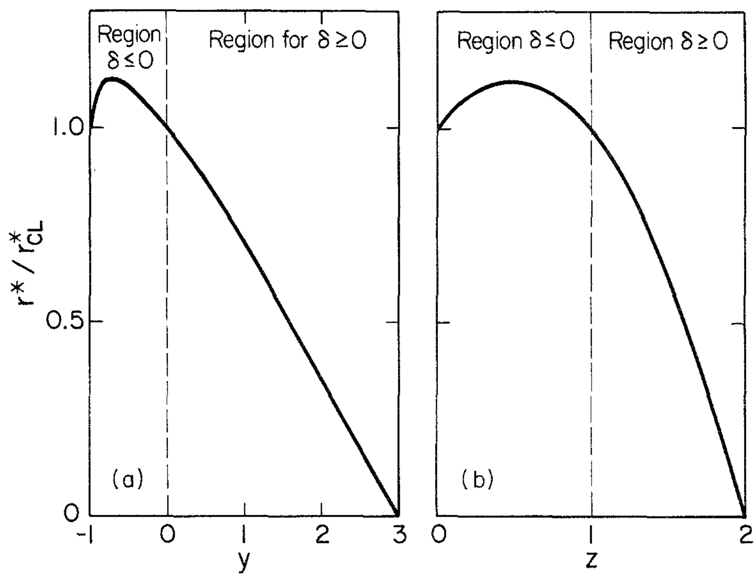


Fig. 2a, b. Plots of the ratio of the Tolman corrected critical radius r^* and the classical critical radius r_{cl}^* versus y and z.

With this definition and with the transformation $z = (1 + y)^{1/2}$ we can transform Eq. (2.5) to

$$r^* = \frac{\sigma}{\Delta\rho\delta\mu}(2 - z)(z + 1) = \tfrac{1}{2}r^*_{\text{cl}}(2 - z)(z + 1) \tag{2.7}$$

where $z \in [0, 2]$ and $y \in [-1, 3]$. Figures 2a, b show the ratio r^*/r^*_{cl} as a function of z and y. The effect of positive δ is to reduce the value of the critical radius. For negative δ the ratio is always greater or equal to 1 and has a maximum at $z = \frac{1}{2}$. The height of the nucleation barrier now becomes

$$(\Delta F)^* = \tfrac{1}{4}(\Delta F_{\text{cl}})^*(z - 2)^4(z + 1)^2$$
$$= (\Delta F_{\text{cl}})^*(r^*/r^*_{\text{cl}})^2(z - 2)^2 \tag{2.8}$$

Figures 3a, b show the ratio $(\Delta F)^*/(\Delta F_{\text{cl}})^*$. We see that a positive δ reduces the height of the nucleation barrier. On the other hand, negative δ increases the nucleation barrier as much as four times.

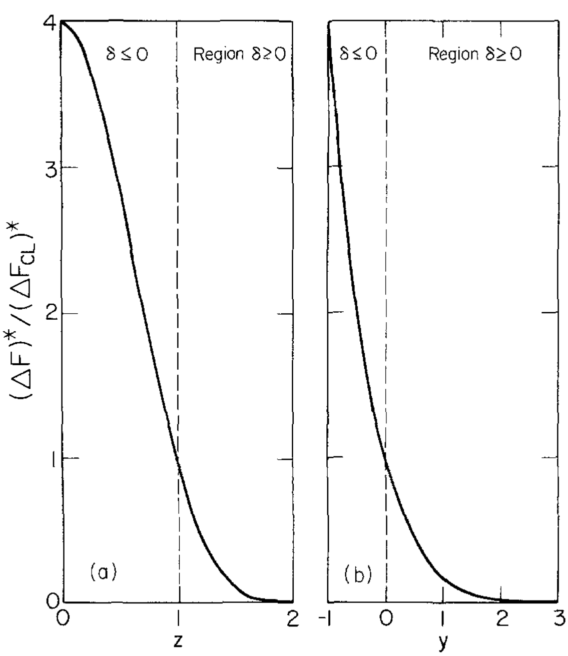


Fig. 3a, b. Plots of the ratio of the Tolman corrected nucleation barrier $(\Delta F)^*$ and the classical nucleation barrier $(\Delta F_{\text{cl}})^*$ versus y and z.

3. THE PARAMETER Y

We assume that

$$\delta = C\xi \tag{3.1}$$

where ξ is the correlation length. We expect C to approach a constant in the critical region. In Eq. (2.6) we defined $y = \delta\Delta\rho\delta\mu/\sigma$. With the above assumption y can be rewritten as

$$y = C\frac{\xi}{\sigma}\Delta\rho\delta\mu \tag{3.2}$$

Using the first approximation

$$\delta\mu = \left(\frac{\partial\mu}{\partial\rho}\right)_T \delta\rho$$

and

$$\delta\rho = \frac{\partial\rho}{\partial T}\delta T \tag{3.3}$$

we obtain

$$y = C\frac{\xi}{\sigma}\left(\frac{\partial\mu}{\partial\rho}\right)_T\left(\frac{\partial\rho}{\partial T}\right)\Delta\rho\delta T \tag{3.4}$$

Near the critical temperature T_c we can use the Fisk–Widom universal amplitude ratio[12] c in Eq. (3.4):

$$\beta^2 c = \frac{[\sigma]}{[\Delta\rho]^2[\xi][g]} \tag{3.5}$$

$[\sigma]$ being the amplitude of the surface tension, $[\Delta\rho]$ of the density difference, $[g]$ of the inverse isothermal compressibility, and $[\xi]$ of the correlation length near T_c. β is the critical exponent characterizing the density difference near T_c. With this amplitude ratio then

$$y = C\frac{1}{2\beta c}\frac{\delta T}{\Delta T_{cx}} \tag{3.6}$$

where $\delta T/\Delta T_{cx}$ is the reduced supercooling. Binder[13] found $\beta^2 c = 0.092 \pm 0.005$ for the universal constant of the surface tension. Using $\beta = 0.34$ we get

$$y = C\,1.85\frac{\delta T}{\Delta T_{cx}}$$

or in the notation

$$x = \frac{\delta T}{\Delta T_{cx}}$$

$$y = C1.85x \tag{3.7}$$

For positive δ we found that $y \in [1,3] \cdot y = 3$ is the limit because then the critical radius is zero. It follows that the reduced supercooling is limited by

$$x \leqslant \frac{1.62}{C} \tag{3.8}$$

in this theory (in other words the Tolman correction breaks down for larger supercoolings) and for negative δ ($y \in [0, 1]$)

$$x \leqslant \frac{0.54}{|C|} \tag{3.9}$$

4. THE REDUCED SUPERCOOLING

We compute now the reduced supercooling. Following the notation of Langer and Schwartz[14] we have

$$\frac{(\Delta F_{\mathrm{cl}})^*}{k_B T_c} = \left(\frac{x_0}{x} \right)^2 \tag{4.1}$$

where

$$x_0^2 = \frac{64\pi}{3\beta^2} \frac{\sigma^3(\partial\rho/\partial\mu)^2}{k_B T_c(\Delta\rho)^4} \tag{4.2}$$

x_0 is believed to be a universal constant and the work of Binder[13] showed that $x_0 = 1.14 \pm 0.1$. The nucleation rate I in the classical Becker–Doering theory is then

$$\frac{I}{V} = J^{\mathrm{BD}} \epsilon_{cx}^{\nu'} \exp\left[-\left(\frac{x_0}{x} \right)^2 \right] \tag{4.3}$$

where

$$\epsilon_{cx} = \frac{T_c - T}{T_c}$$

and ν' a critical exponent assumed to be equal to 0.63 in this theory. The value for J^{BD} is given in Table I. There are some doubts about the kinetical prefactor, therefore we generalize the prefactor to

$$J^{BD} \epsilon_{cx}^{g\nu'}$$

Table I. Values of Various Parameters. The Parameters a and b are based on CO_2 as well as J^{BD}.

x_0	1.14 ± 0.1	Binder[13]
$\beta^2 c$	0.092 ± 0.005	Binder[13]
ν'	0.63	
j^{BD}	$5.81 \times 10^{33}\ \text{cm}^{-3}\ \text{sec}^{-1}$	
$a(I/V=1)$	0.1308 °K	
$a(I/V=10^5)$	0.1401 °K	
$b(I/V=1)$	0.0081 °K	
$b(I/V=10^5)$	0.0095 °K	

with a free parameter g. Substituting ΔF for ΔF_{cl} in Eq. (4.3) and solving for the reduced supercooling one obtains

$$x = \frac{1}{C1.85}\left\{\left[\frac{4+e}{2} \pm \frac{1}{2}\left(e^2+4e\right)^{1/2}\right]^2 - 1\right\} \tag{4.4}$$

with

$$\begin{aligned} e &= \frac{2}{C1.85}\,\frac{\left(1+gb\ln\epsilon_{cx}\right)^{1/2}}{a} \\ a &= \frac{x_0}{\left[\ln\left(VJ^{BD}/I\right)\right]^{1/2}} \\ b &= \frac{\nu'}{\ln\left(VJ^{BD}/I\right)}\,. \end{aligned} \tag{4.5}$$

Values for the parameters a and b for different ratios I/V are listed in Table I. For positive δ we have to take the minus sign and for negative δ the plus sign in Eq. (4.4). In the limit $\delta \to 0$ we find the classical result

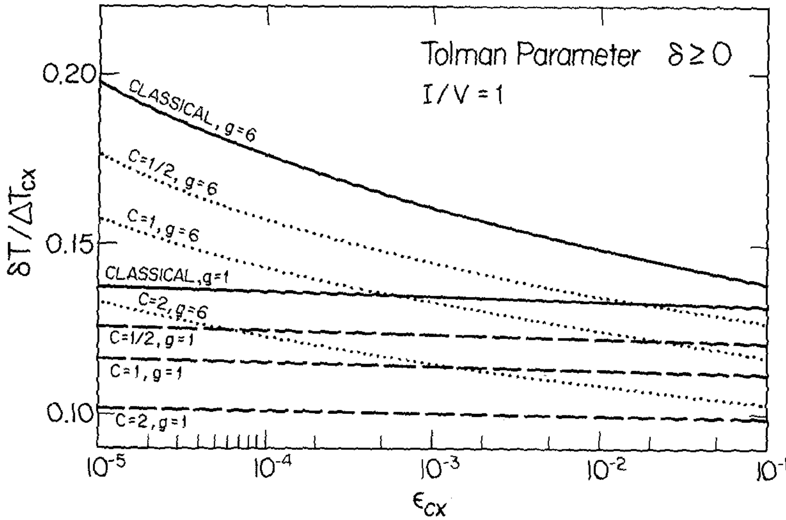
$$x = \frac{a}{\left(1+gb\ln\epsilon_{cx}\right)^{1/2}} \tag{4.6}$$

In formula (4.4) we neglected the correction to the prefactor

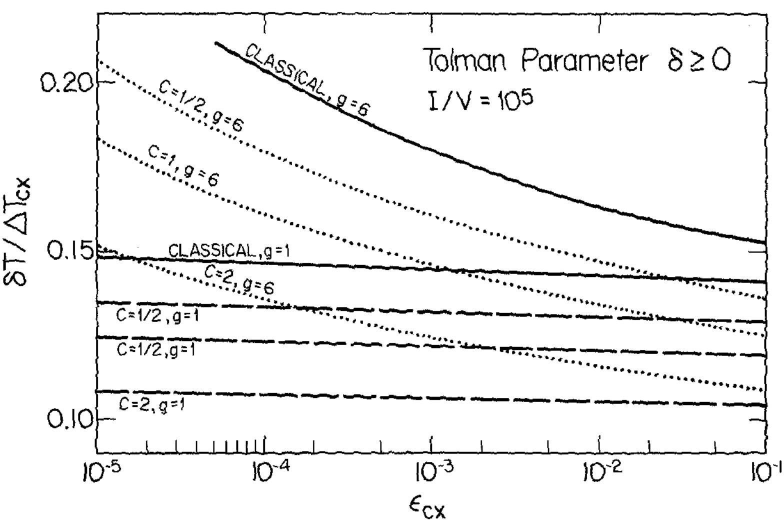
$$J^{BD}\left[(z-2)^2 z\right]^{1/2}$$

which can be shown to be negligible.

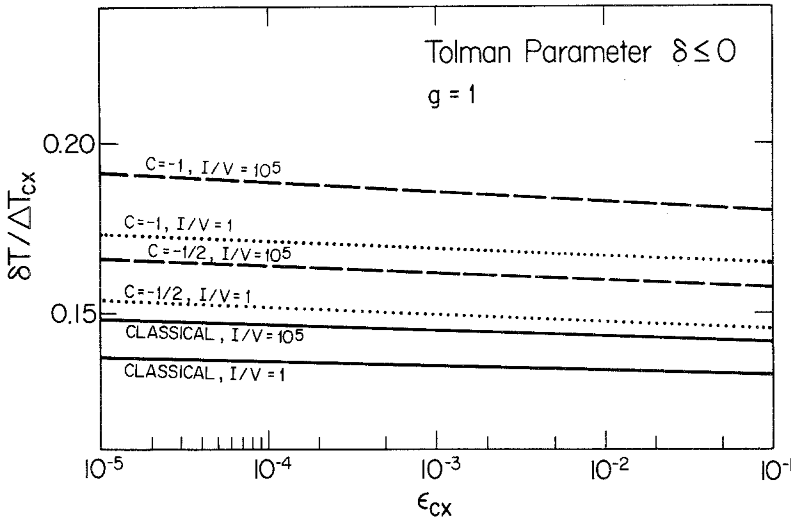
From the Figures 4a, b, c, d it is seen that the introduction of the Tolman correction in the classical and generalized version of the nucleation theory does not result in a qualitative change in the slope of the curve of the reduced supercooling as a function of ϵ_{cx} at constant nucleation rates. The Tolman parameter δ therefore seems to be a suitable parameter to fit future measurements on nucleation rates.


Tolman Parameter δ ≥ 0
I/V = 1
CLASSICAL, g=6
C=1/2, g=6
C=1, g=6
CLASSICAL, g=1
C=2, g=6
C=1/2, g=1
C=1, g=1
C=2, g=1
0.20
0.15
0.10
δT/ΔTcx
10-5
10-4
10-3
10-2
10-1
εcx

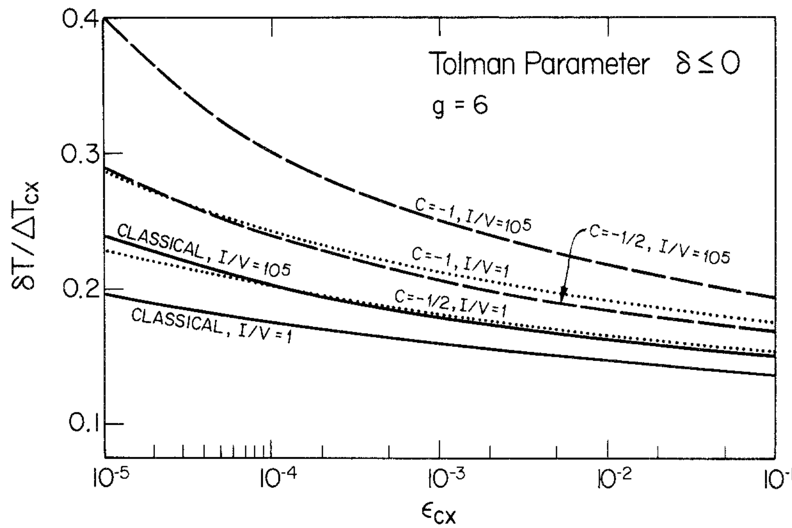
a


Tolman Parameter δ ≥ 0
I/V = 105
CLASSICAL, g=6
C=1/2, g=6
C=1, g=6
CLASSICAL, g=1
C=2, g=6
C=1/2, g=1
C=1/2, g=1
C=2, g=1
0.20
0.15
0.10
δT/ΔTcx
10-5
10-4
10-3
10-2
10-1
εcx

b



c



d

Fig. 4a, b, c, d. Plot of the reduced supercooling x versus $\epsilon_{cx} = (T_c - T)/T_c$ for various positive values of the Tolman parameter for $I/V = 1$ (part a) and $I/V = 10^5$ (part b). Plot of the reduced supercooling x versus $\epsilon_{cx} = (T_c - T)T_c$ for various negative values of the Tolman parameter for the classical prefactor (part c) and the generalized prefactor (part d).

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