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NUCLEATION THEORY AND DYNAMICS OF FIRST-ORDER PHASE TRANSITIONS NEAR A CRITICAL POINT

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Abstract.- A brief review of nucleation theory and its problems is given. Main emphasis is on nucleation close to the critical point of liquid-gas systems or liquid-liquid mixtures, and the interpretation of recent experiments in these systems. It is shown that critical slowing down leads to considerable enhancement of the relative undercooling at the limit of metastability close to the critical point. The role of pre-exponential factors on the nucleation rate is discussed, and scaling laws for nucleation near the critical point are derived. Computer simulations of the lattice gas model are used to show that the one-cluster-coordinate theory is sufficient even close to the critical point and that the classical "capillarity approximation" underestimates the energy barriers even at fairly low temperatures.

1. Introduction.- Nucleation theory considers the rate of phase transformation of metastable states. The mechanism one has in mind is the formation of small nuclei of the new (stable) phase by thermal fluctuations. These nuclei then grow to form large macroscopic domains of this new phase.

In a liquid-gas system, such initially metastable states can in principle be produced by quenching the system from a temperature in the one-phase region to a point within the co-existence curve, keeping the density constant (Fig.1A). Similar quenches can be performed in liquid or solid mixtures (Fig.1B). Very beautiful experiments of this type have in fact been performed by Goldburg and coworkers /1,2/ and by Knobler and others /3-6/, and will be described in the next section. The present paper will be largely concerned with the theoretical interpretation of these experiments, emphasizing the regime close to the critical point T_c. The reason is that varying the temperature T and hence the parameter ε = ΔT/TC = (T_c-T)/T_c changes the relevant time scales (because of "critical slowing down" /7/), and hence a more stringent test of the theory is possible than with ordinary nucleation experiments (done far away from T_c). In fluid systems away from T_c the attempt frequency is so high that nucleation becomes appreciable whenever the energy barrier becomes less than about 50 k_BT. For such high barriers the conventional Becker-Döring nucleation theory /8/ is a reasonable approximation, and typically the limited accuracy of experimental data does not warrant to consider a more sophisticated theory. In solid systems, on the other hand, the atomic mobility is much smaller and hence the energy barriers relevant for the observation of homogeneous nucleation would be much smaller. But there in most cases...
heterogeneous nucleation" (at lattice defects, surfaces etc.) is more important.

The situation is also more complicated since anisotropy energy, elastic energy etc. have to be included when discussing the formation energy of a nucleus. Therefore, only fluid systems will be considered explicitly in the present paper, but the general concepts are clearly more general.

As far as static properties near the critical point $T_c$ are concerned, all liquids as well as liquid mixtures belong to the same "universality class" /9/. Even nonequilibrium systems as the electron-hole liquid, which occurs in semiconductors at very low temperatures /10/ (Fig. 2), should belong to the same class. "Universality" means that parameters describing the singular behavior near the critical point, like critical exponents, scaling functions etc. are the same for all systems belonging to the same class, which in our case is the class of the Ising or lattice gas model. Hence one can also expect that the same description of large droplets (or "clusters") applies near the critical point in all these systems. Thus we will use "computer experiments" /11/ on lattice gases, which are so much easier to perform than computer experiments on more realistic systems, in order to check the assumptions made in the theory which is outlined below.

2. Experimental situation.- The experiments usually are started in a thermal equilibrium one-phase state outside the coexistence curve. In a sudden quench the system is brought to a point inside the coexistence curve, where thermal equilibrium would require a first-order phase transition to a mixture of macroscopic domains of the two stable phases. (In practice this is done e.g. for mixtures with an inverted miscibility gap, where the "quench" is a sudden rise of temperature produced by microwave heating). One then asks whether for a considered undercooling $\delta T$ an appreciable fraction of the metastable phase transforms within a characteristic time $\tau_{\text{cond}}$ [e.g., whether an appreciable fraction of supersaturated gas has condensed]. In these thermal equilibrium nucleation experiments the time $\tau_{\text{cond}}$ is typically of the order of 1 s. A very different regime of times would be accessible in laser-induced nucleation in solids [$\tau \approx 10^{-9}$ s], but, in that case, one no longer deals with thermal equilibrium. In the equilibrium case, the undercooling $\delta T$ where appreciable phase transformation sets in can be measured by light scattering, direct microscopic observation or measuring the latent heat which is associated with the condensation. Varying the density of the fluid, or the concentration of the mixture, one can measure this relative undercooling $\delta T/\Delta T$, where the phase transformation starts to occur within $\tau_{\text{cond}}=1$ s, for various $\epsilon$ (figure 3).

![Fig. 2: "Phase diagram" of the (nonequilibrium) electron-hole-gas-liquid system in Ge (Temperature plotted versus carrier density, according reference /10/). Open and full circles denote various experimental data (see /10/ while full curve is a theoretical interpretation derived from equation (17)/10/.

![Fig. 3: Relative undercooling $\delta T/\Delta T$ vs. $\delta T/T_c$ at which the phase transformation occurs during $\tau_{\text{cond}}=1$ sec, plotted versus distance from the critical point. Circles denote data for lutidine-water mixtures /1/, squares C$_2$H$_4$-C$_7$F$_{14}$ mixtures /4/, crosses $^3$He/5/ and triangles CO$_2$/6/.

Dashed curve is the result of "classical" nucleation theory while dash-dotted curve is the prediction of /13/. From reference /1/.
Various systems like lutidine-water mixtures (circles) /1/, C7H15-C7F14 mixtures /4/ (squares), He /5/ (crosses) and CO2 /6/ (triangles) fall within error bars on the same universal curve, which is a constant far away from Tc, but rises steeply close to Tc. All these authors /1-6/ have taken all precautions against heterogeneous nucleation; thus one can be relatively sure that this behaviour is characteristic of homogeneous nucleation. The theoretical analysis which will be given below will show that what is measured here is some sort of universal dynamic scaling function for this highly nonlinear dynamic response of the system.

The curves included in the figure are theoretical predictions. The dashed horizontal curve is the "classical" Becker-Döring nucleation theory, as adapted to the critical region by Langer and Turski /12/. Note that corrections discussed in the nucleation literature over decades such as Lothe-Pound translation-rotation corrections /8/, replacement partition function corrections /9/ etc. would not change much-the agreement with experiment would become even worse. The dash-dotted curve is the prediction which follows from the theory developed by Stauffer and the present author /13/. Although the agreement is not perfect, the theory does give the right trend. Note that in neither calculation are there adjustable parameters.

Next, the basic ingredients of this theory /13/ will be outlined, and the open questions will be pointed out. It will be shown that lack of knowledge on the free energy barriers of the "critical clusters" still hamper the calculation of this dynamic scaling function of nucleation rates. It is this point where computer simulations on lattice gases are helpful. In the last part of this paper, hence, the direct simulation of the equilibrium between a cluster and surrounding supersaturated gas will be briefly discussed.

3. Nucleation theory and its check up by computer experiments.- As is well known, homogeneous nucleation is a thermally activate process where clusters exceeding a certain critical size have to be formed in order to enable the phase transformation to occur. Let us describe all clusters by a certain set of coordinates: their "size" \( l \) [i.e., the amount of order parameter associated with a cluster], their surface area \( s \), etc. Then the formation free energy \( F(l, s, \ldots) \) of a cluster in the metastable state will exhibit a saddle point geometry (Fig.4): for small clusters the surface area is relatively large, and although their bulk energy is negative, \( F \) is still positive due to unfavorable surface energy. For large clusters, the negative bulk energy wins, and hence \( F \) is steadily decreasing there.

![Fig.4.-Schematic plot of the variation of the cluster formation free energy \( F(l, s) \) as a function of two "cluster coordinates" (e.g., size \( l \) and excess surface area \( s-s_{\text{min}} \)). The coordinates of the saddle point are denoted by \( \tilde{l} \).](image)

Steady-state nucleation is then described /13/ by equations equivalent to Maxwell’s equations for steady-state currents in the "cluster-size space" \( \{l, s, \ldots\} \):

\[
\begin{align*}
\nabla \times \mathbf{E}(\tilde{l}) &= 0, \\
\epsilon \nabla^2 \phi(\tilde{l}) &= 0.
\end{align*}
\]

(1)

and the continuity equation:

\[
\nabla \cdot \mathbf{J}(\tilde{l}) = 0.
\]

(2)

Here the "field" is:

\[
\mathbf{E}(\tilde{l}) = -\nabla \phi,
\]

(3)

with a potential:

\[
\phi = -\ln(\tilde{n}(\tilde{l})/n(\tilde{l})),
\]

(4)

where \( \tilde{n}(\tilde{l}) \) is the cluster concentration which is established in the steady state nucleation process, and \( n(\tilde{l}) \) is defined by the Boltzmann factor:
\[ n_j = \exp \left[ - \frac{F_j}{k_B T} \right]. \]  
\[ (5) \]
This is a hypothetical cluster concentration which would be in equilibrium in the metastable state.

For the current density \( \dot{j}(\hat{z}) \) we then have the relation involving a "conductivity tensor" \( \sigma(\hat{z}) \):

\[ \dot{J}(\hat{z}) = \sigma(\hat{z}) \mathbf{E}(\hat{z}) = n(\hat{z}) R(\hat{z}) \mathbf{E}(\hat{z}) = n(\hat{z}) R(\hat{z}) \frac{n(\hat{z})}{n(\hat{z})} \cdot \]
\[ (6) \]
Here \( R(\hat{z}) \) is a tensor of cluster reaction rates describing purely kinetic factors. This set of equations is completed by specifying boundary conditions for the potential. Since small clusters are in thermal equilibrium, we have:

\[ \phi(0) = -\frac{n(0)}{n(0)} = -1. \]  
\[ (7) \]
Further, since there are not yet any infinitely large domains present, we have:

\[ \phi(\hat{z} = \infty) = 0. \]  
\[ (8) \]
The nucleation rate is then the total current in large distances from the "source" at the origin:

\[ J = \int_{\hat{z}} \dot{j}(\hat{z}) d\hat{z}. \]  
\[ (9) \]
Just as a battery supplies electrons to maintain an electric current, thermal fluctuations supply small clusters (in this continuum description at \( \hat{z} = 0 \)) which are fed into the nucleation process and maintain the steady-state nucleation current.

This description is the more accurate the more cluster coordinates are used. However, the problem with this approach is twofold: (i) the functions \( n(\hat{z}), R(\hat{z}) \) are not known explicitly very well; (ii) even if they were known, the problem is nontrivial, since there is no general solution for conduction in an inhomogeneous and anisotropic medium. What one can do is a saddle point approximation appropriate for \( F(\hat{z}) \gg k_B T \): one expands \( F(\hat{z}) \) at the saddle point \( \hat{z}_S \) up to quadratic terms:

\[ F(\hat{z}) = F(\hat{z}_S) + (\hat{z} - \hat{z}_S) g(\hat{z} - \hat{z}_S) + \ldots \]  
\[ (10) \]
The matrix \( g \) has one negative eigenvalue \((-g)\) and otherwise positive ones, since \( \hat{z}_S \) is a saddle point. Introducing an effective cross section area \( \hat{A}_S \) of the saddle point region, one finds the following Arrhenius formula /13/:

\[ J = \exp(-\frac{F(\hat{z}_S)}{k_B T} \sqrt{g} \left( \frac{\hat{A}_S (\hat{z}_S)^2}{\hat{A}_S} \right) / k_B T). \]  
\[ (11) \]
In the conventional Becker-Döring nucleation theory, one uses a single cluster coordinate \( \hat{z} \) only, i.e. all properties of the clusters are uniquely fixed by their size, fluctuations in the cluster properties to be described by other coordinates being neglected. With one coordinate only, the steady-state solution for both \( \hat{A}(\hat{z})/n(\hat{z}) \) and \( J \) is easily found. It reads:

\[ \frac{\hat{A}(\hat{z})/n(\hat{z})}{J} = J \int_{\hat{z}} \frac{R(\hat{z}^\prime)n(\hat{z}^\prime)}{J} d\hat{z}^\prime, \]  
\[ (12) \]
and:

\[ J = \left[ \int_0^\infty \frac{d\hat{z}}{R(\hat{z}) n(\hat{z})} \right]^{-1}. \]  
\[ (13) \]
The saddle point approximation to this formula (quadratic expansion at the "critical cluster size" \( \hat{z}_S \)):

\[ J \approx R(\hat{z}_S) \sqrt{g} \exp(-\frac{F(\hat{z}_S)}{k_B T}), \]  
\[ (14) \]
yields a similar expression as above, but the preexponential factor is different: with one coordinate one does not take properly the available phase space into account. We conclude that fluctuations will affect the preexponential factor of the nucleation rate.

The question is, how serious is this neglect in practice, and how accurate is the one-cluster-coordinate nucleation theory? This is a question which can be answered from Monte Carlo simulations of the two-dimensional lattice gas model. These atoms are restricted to occupy sites of a given lattice (e.g., the square lattice). Atoms which are nearest neighbors attract each other and, in addition, there may be a binding energy to the lattice or substrate, if one considers the lattice to be constituted by the "absorption sites" produced by the surface layer of an underlying substrate lattice. This is also a crude model of crystal growth from the gas phase in the limit where the crystal grows by layer by layer addition. First of all, one has to obtain the functions \( R(\hat{z}) \) and \( n(\hat{z}) \) which occur in the integrals in equations (12), (13), figure 5. It turns out that the data are quite well approximated by a power law for
Note that in figure 5 also the "classical" Becker-Döring "capillarity approximation" is included. There, one assumes that the surface free energy of the droplets is precisely obtained by using the surface tension $f_S$ of an infinite flat surface, and hence:

$$n(t) = n(1) \exp\left(-f_S \frac{S_e}{2} \Delta \mu k_B T\right), \quad (18)$$

where $S_e$ is the surface area of a droplet (assumed spherical in the classical theory).

In the two dimensional lattice gas, $f_S$ is known rigorously from Onsager's exact solution /15/, and hence equation (18) can be evaluated unambiguously. Obviously, it does not fit the computer experiment "data" in the considered range of cluster sizes. One does expect, however, that this classical expression becomes valid asymptotically for very large clusters. In the direct simulation, where one just counts the actual average numbers of clusters of all sizes, one cannot go to such large cluster sizes, however, since these very large clusters are too seldom. Hence, later on, another method of simulation will be reported where such large critical clusters are studied directly. The present cluster sizes in figure 5 are relevant for energy barriers $F_{x/k_B T} \ll 10$ or less; there, distinct deviations from classical theory do occur.

The "data" of figure 5 now provide the input necessary to evaluate unambiguously the nucleation rate as well a steady-state cluster distribution [Eqs. (12), (13)]. On the other hand, one may record the actual $R(t)$ which occurs in the simulation; since then there are no adjustable parameters whatsoever, one obtains a meaningful comparison between computer experiment and the one-cluster-coordinate nucleation theory.

Figure 6 shows the outcome of the computer experiment. Cluster concentrations $R_i(t)$ are plotted versus time $t$, the parameter of the curves is the cluster size $i$. Three different quenches are shown. After some time lag, the cluster concentrations always reach some nearly stationary state. In these flat parts, the cluster concentrations do not fit the equation of state of the electron-hole droplet system (Fig. 2).
Average cluster concentration $\bar{n}_i(t)$ of the two-dimensional lattice gas model at $T = 0.96 T$, plotted versus time after quenches from $H_0 = 0$ to $H_0 = 0.03$ (a), 0.024 (b) and 0.016 (c). Parameter of the curves is $t$. Relaxation time in equilibrium ($\tau_{rel}$) as well as time-scale for the first-order phase transition ($\tau_{\Delta H}$) are indicated. From /13/.

become truly constant, but decrease slowly: this happens partly because of the neglected cluster coagulation events, and partly because the "supersaturation" of the lattice gas decreases by cluster formation, and thus also concentrations of small clusters change with time. Anyhow, we may take the flat parts at least as rough estimates of what the steady state values should be.

Figure 6 now compares the "observed" values (points) to the calculations using equations (12), (13) [broken curves]. Since there are no adjustable parameters, not even in the coordinate scales, one does in fact get significant agreement, fitting not only one curve but a whole family of curves for liquids near their critical point, since they belong to the same static universality class.

6. Scaling laws for nucleation near a critical point. - What is known about the general behavior of the cluster concentration $n(t)$ and reaction rate $R(t)$ near $T_c$? As for other quantities near $T_c/\delta$, one can write down "scaling expressions": these functions do not depend on the three variables $t$, $\epsilon$, and $\Delta u$ separately, but apart from a "scale factor" - only on two scaled variables $\Delta u^{1+x}$, $\epsilon t^y$, where the scaling powers $x$, $y$ are obtained from /13/ $x = 1, y = 1/\beta \delta$:

$$n(t) = q^{-2(1+\delta)} \frac{\Delta u^{1/\beta \delta}}{\epsilon t^y} , \quad (19)$$

$$R(t) = \frac{q^{-2-\nu z/\beta \delta}}{\epsilon t^{1-\beta \delta}} . \quad (20)$$

Both the exponent $(2+1/\delta)$ of the "scale factor" and the exponents $x$, $y$ are obtained
by considering the contribution of the clusters to the free energy; nucleation theory considers clusters much larger than the correlation length $\xi$ (Fig. 8), which are basically non-interacting apart from random collisions where the considered cluster reactions take place. Hence the contribution of

$$p = p_0 + k_B T \sum n_{\xi},$$

where $p_0$ is a "background" term (which also contains the contribution of the more strongly interacting clusters of the scale of the correlation length $\xi$ or smaller). We require now that both $p_0$ and the cluster contribution to the pressure have the same scaling behaviour as $p$ itself, i.e. its singular part $p_{\text{sing}}$ must scale as:

$$p_{\text{sing}} = \varepsilon^{\beta(\delta+1)/\beta} \left( \Delta \mu / \varepsilon^{1/\delta} \right).$$

Combining equations (21) and (22) sets the exponents to be used in equation (19), but does not determine the explicit structure of the "scaling function" $N$. But since two scale factors $q$ and $b$ have been taken out, one can invoke the universality principle to conclude that $N$ should be universal (i.e., the same for all fluids including the three dimensional lattice gas). By a similar argument, one can relate $R(\xi)$ to the dynamic response of the system in equilibrium states, and invoke "dynamic scaling" to obtain the scaling behavior of $R(\xi)$ as given in equation (20). Clearly, the power-law prefactors of equations (19) and (20) have dominated the behavior of $R(\xi)$ and $n(\xi)$ in the simulations (Fig. 5).

Let us examine the explicit expressions of the previous section in the light of this general scaling analysis. The reaction rate, equation (15), is indeed a special case of the scaling assumption, equation (20) [with $R=1$]; similarly, the Fisher droplet model [Eq. (17)] is a special case of equation (19) with $N = \exp(-\varepsilon^{1/\delta} - \Delta \mu / \varepsilon^{1/\delta})$.

The classical expression, equation (18), on the other hand, is not fully consistent with scaling. To examine this point further we have to express the surface area $S_\xi$ in terms of $\xi$, the amount of order parameter associated with a cluster of volume $V_\xi$. For compact clusters we have, in $d$ dimension, $S_\xi = S V_\xi^{1/\delta}$, where $S$ is a constant of order unity. From figure 3 we note:

$$\xi = V_\xi (p_{\text{liquid}} - p_{\text{gas}}) = V_\xi \beta \varepsilon^{1/\delta},$$

where $\beta$ is a constant, and hence $S_\xi = \varepsilon^{\beta(\delta+1)/\beta} \left( \Delta \mu / \beta \varepsilon^{1/\delta} \right) \xi^{1-1/\delta}$.

Fig. 9.- Scaled relaxation time of the first-order phase transition in the two dimensional lattice gas model plotted versus scaled supersaturation. Points are simulation results (for $\varepsilon \approx 0.1, 0.04$ and $0.02$, respectively), while curve is a theoretical formula analogous to equation (32). From /18/.

Making use of the critical behaviour of the surface tension $\varepsilon = \tilde{\varepsilon} (d-1)^{\nu}$, where $\tilde{\varepsilon}$ is a constant, we hence find:

$$T^{(1)} = \frac{\beta \varepsilon^{1/\delta}}{\Delta \mu / \beta \varepsilon^{1/\delta}}.$$
\[ n(t) = n(1) \exp \left[ (d-1) \sqrt{S_{\Delta u}} - \Delta u \right] = n(1) \exp \left[ -\left( \frac{\delta u}{b} \right) \left( 1 - \frac{\delta u}{b} \right) \left( \gamma \right) \right], \tag{24} \]

where in the last step the scaling law \( d = 2 + \varepsilon / 3 \) was used. Thus we note that the exponential in equation (24) has the correct scaling form - but the preexponential scaling power \( \Delta u - (2+1/6) \) is missing! Hence, classical nucleation theory, in its standard form, cannot provide us with the correct critical behavior of the nucleation rates.

The general scaling expressions for \( n(t) \) and \( R(t) \) can be used to derive general scaling laws for the nucleation rate, however. From equations (13), (19), and (20) we find

\[ J = \int_0^t \frac{d\gamma}{d\tau} \left[ \frac{\Delta u}{b c} \right] \left( 1 - \frac{\Delta u}{b c} \right)^{1/2} \left( \frac{R(t')}{\Delta u} \right)^{3/2} \left( \frac{\Delta u}{b c} \right) \left[ \frac{R(t')}{\Delta u} \right]^{-1/2} \exp \left[ -x_{\text{class}} \left( \frac{\Delta u}{b c} \right) \right]. \tag{25} \]

Hence, it turns out that the nucleation rate depends on the chemical potential difference and hence on the supersaturation in the same scaled form \( \Delta u - (2+1/6) \) as the equation of state, equation (22):

\[ J = \frac{3}{2} \frac{\gamma}{\Delta u} \left( \frac{\Delta u}{b c} \right) \] 

where \( \gamma \) is again (another) universal function of its argument.

A simple explicit estimate of \( J \) is obtained by amending the classical expression for the droplet concentration, Eq. (24) with the scaling power \( \Delta u - (2+1/6) \) which should occur in any scaled expression for the droplet concentration. One then finds /13/:

\[ J = \frac{3}{2} \Delta u \left( \frac{\Delta u}{b c} \right)^{3/2} \exp \left[ -x_{\text{class}} \left( \frac{\Delta u}{b c} \right) \right]. \tag{29} \]

where the universal constant \( x_{\text{class}} \approx 0.7 \) [as estimated from surface tension measurements]. Due to the use of the saddle point approximation [ Eq. (14)] Eq. (29) is accurate for small \( \Delta u / b c \) only, but the above approximation for \( n(t) \) and \( R(t) \) is not expected to yield accurate results for large \( \Delta u / b c \). It was equation (29), however, which was used in the comparison to the data (Fig. 3) and hence it is not too surprising that systematic deviations between theory and experiment occur for larger \( \Delta u / b c \).

Before discussing on how one can make progress to better determine the scaling function \( J \), let us note that it is actually \( \frac{\delta p(t)}{\rho_{\text{liquid}} \gamma} \) which is measured: one must measure the time \( t_{\text{cond}} \) after which an appreciable fraction of the metastable supersaturated phase is "condensed." This fraction is, for a liquid-gas system:

\[ \frac{\delta p(t)}{\rho_{\text{liquid}} \gamma} = \frac{t}{\tau} \int_0^t \frac{J(t') \delta t}{3} \left[ R(t-t') \right]^3 \tag{30} \]

where \( R(t-t') \) is the radius of a droplet at
time t which was nucleated at time $t'$ after
the quench. Neglecting the decrease of su-
persaturation during the phase transforma-
tion, one has $J(t) \approx J$ and $R(t-t') = R^\infty + \frac{\xi}{\Delta T} D(t-t')$, where $D$ is the diffusion
coefficient $[D = \frac{\beta \nu}{2}]$ and $R^\infty$ the size of the
critical nucleus. However, neglecting $R^\infty$, one finds:

$$\frac{\delta \rho(t)}{\rho_{\text{liquid}}} = \frac{8 \pi}{15} J \left[ \frac{\beta \nu}{\Delta T} D \right]^{3/2} t^{5/2}. \quad (31)$$

The condensation time $\tau_{\text{cond}}$ is defined when
the reaction reaches completion, i.e. when
the left hand side of equation (31) is of
order unity. Thus, it follows that $/13/$:

$$\tau_{\text{cond}}^{-1} = 3^n \left\{ \frac{8 \pi}{15} J \left[ \frac{\beta \nu}{\Delta T} D \right]^{3/2} \frac{\xi}{\Delta T} \right\}^{2.5}.$$ \quad (32)

It is this formula which [for $\tau_{\text{cond}} = 1$ s and using equation (29) for $\rho_{\text{gas}}$] was compared
to experiment in figure 3. Langer and
Schwartz /17/ recently pointed out that the
agreement between theory and experiment
becomes better, when one does neglect nei-
ther $R^\infty$ nor the decrease of supersaturation
during the droplet formation. However, the
uncertainty about preexponential factors
in the scaling function $\bar{J}(\xi)$ is not re-
moved by this analysis. On the other hand,
a treatment similar to the above equations
(30) to (32) has been applied to the rela-
xation of the two dimensional lattice gas
/18/, figure 9. In that case, $n(t)$ was well-
represented by equation (17), and hence
there was no ambiguity in calculating $\bar{J}$
$\frac{\Delta \mu/(\beta \nu)^{1/2}}{\rho_{\text{gas}}}$ from equation (13), (17). It
turns out that the computer experiment da-
ta have the expected dynamic scaling pro-
property, and moreover they agree nicely with
the predicted scaling function for the re-
lexation time. Hence, basically the same
approach works for both two dimensional
lattice gases (Fig.9) and for three dimen-
sional real fluids and fluid mixtures
(Fig.3).

5. Corrections to the Classical "Capilliarity
Approximation" for the Droplet Forma-
tion Free Energy. - Let us now come back to

the physical origin of the correction fac-
tors which modify the classical expression
for the droplet concentration, equation (18),
near a critical point. Consider critical
clusters which are not much larger than the
correlation length $\xi$ of order parameter
fluctuations (Fig.8). Since the thickness
of the droplet-gas interface is also given by
$\xi$, a distinction between bulk and surface
of a cluster then becomes questionable.
Hence, there is no reason to assume that the
classical expression for the droplet free
energy is still correct if we deal with
such strongly fluctuating (partially "rami-
field") clusters. Of course, one can still
define an effective surface free energy of
the cluster by writing:

$$F(\xi) = \Delta \mu + \tilde{F}_{\text{surf}}(\xi),$$ \quad (33)

but $\tilde{F}_{\text{surf}}(\xi)$ is no longer proportional to
$\nu - 1/\rho_{\text{gas}}$ as the cluster size decreases; rather, one expects a "crossover" as shown
schematically in figure 10.

Fig.10. - Schematic plot of effective cluster surface
free energy $F_{\text{surf}}(\xi)$ plotted versus $\nu^{-1/\rho_{\text{gas}}}$. Crosso-
er from the classical regime, where mean fluctua-
tion of cluster surface area is small as compared
to the mean cluster surface area, to the nonclassi-
cal strongly fluctuating regime is indicated.

For $\nu \approx \nu_{\text{crit}}$, we must have $F_{\text{surf}}(\xi)$ of the
order of the thermal energy $k_B T$, because
such clusters are typical for that tempera-
ture (i.e., forming spontaneously in fairly
high concentration). Asymptotically for
The classical expression is reached, i.e., $F_{\text{surf}}^{\text{eff}}(\xi) = \left(\frac{V_f}{\xi^d}\right)^{1-1/d}$. A crossover away from the classical expression sets already in at $V_f = V_{\text{cross}}$ where $F_{\text{surf}}^{\text{eff}}(\xi)$ differs from the classical value by, say, 10% (note that the famous rotation-translation correction factor $10^{17}$ to the nucleation rate is removed if one changes the surface tension by about 15%). In looking for preexponential correction factors to the classical expression, deviations of a few percent do matter effectively in this crossover regime, fluctuations in the surface area start to become comparable to the surface area itself. The description given qualitatively in figure 10, also applies far away from the critical point, where $\xi$ is of the order of the distance between neighboring atoms. But, while near $T_c$ the function $F_{\text{surf}}^{\text{eff}}(\xi)$ is universal (apart from scale factors), far away from $T_c$ the deviations from the classical expression for small cluster sizes reflect details of the potential between neighboring atoms, and hence depend on the material considered: no "universal" description is then possible.

Recently a simulation method has been developed by which one can study $F_{\text{surf}}^{\text{eff}}(\xi)$ more directly in this crossover regime. This is done by putting a liquid cluster into a finite box and by studying the resulting equilibrium between the cluster and the surrounding supersaturated gas in the box (Fig. 11). This approach differs from some previous attempts along similar lines where all the atoms in the box were considered as part of the cluster: such a treatment is reasonable only if the gas density is less than about $10^{-3}$ of the liquid density, because then the supersaturated gas does not contribute much to the total free energy of the box, and no serious error in $F_{\text{surf}}^{\text{eff}}(\xi)$ is introduced. For higher gas densities, however, the error does become serious and hence the new method of Reference should be used.

The equilibrium is described qualitatively in figure 12. Here the free energy of the total system (cluster + gas) is shown as a function of cluster size $\xi$ and chemical potential difference. Since the total particle number in the box is held constant, the system is constrained to move on the dash-dotted curve. This is the reason why the resulting equilibrium is stable rather than unstable: if the cluster is small, most of the particles are in the gas phase; although the barrier is low, the total free energy is high. Conversely, if the supersaturation is very small and the cluster is large, the free energy of the gas is small but the barrier is high. Hence in between there is a relatively more favorable situation, where the cluster is in stable equilibrium with the surrounding gas: although the barrier is low, the total free energy is high. A detailed analysis of the situation shown in figure 12 yields the result that the equilibrium is obtained for:

$$\frac{\partial F_{\text{surf}}^{\text{eff}}(\xi)}{\partial \xi} = \Delta \mu (1 - \rho_{\text{gas}}/\rho_{\text{liquid}}).$$  (34)
Fig. 12.- Schematic plot of the free energy of the box (Fig. 11) plotted versus size \( R \) of the cluster and chemical potential \( \mu \). Free energy of the gas is indicated by dashed straight line. Due to constraint of constant total particle number the system is constrained to move on dash-dotted curve /19/.

Hence, one just observes in the simulation which cluster size \( \xi^* \) is in equilibrium with which chemical potential difference \( \Delta \mu \) from equation (34) one then reads off \( \partial \mu^{\text{eff}} \) /\( \partial \xi^* \). Varying \( N/V \) one varies the size \( \xi^* \) at which equilibrium is obtained. Figure 13 shows some results which were obtained with this technique for the two dimensional lattice gas. Circles are the result of the simulation at \( T/T_c \approx 0.59 \), the broken curve is the prediction of classical theory. Crosses are more accurate estimates from low temperature expansions /19/, which are available for very small cluster sizes only. The full curve was obtained by integrating the cluster internal energy from zero temperature to the considered temperature. This indirect method agrees well with the direct results based on equation (34), and proves the consistency of the various numerical procedures. Although the data are no longer in the region near the critical point here, classical theory still predicts values of \( \mu^{\text{eff}} \) which are too small and, hence, too small energy barriers for most of the cluster sizes studied. This discrepancy goes in the same direction as the power law correction applicable near \( T_c \).

It remains an open question, however: to what extent similar deviations occur in realistic three dimensional systems far away from \( T_c \)?

6. Conclusions.- In this paper it was asked: does homogeneous nucleation theory provide us with an accurate description of first order transition kinetics? First, it was shown that the classical one-cluster-coordinate nucleation theory, where fluctuations in cluster properties are neglected, may yield inaccurate preexponential factors. Computer simulations of the lattice gas model show that, even near the critical point, the one-cluster-coordinate nucleation theory is quite sufficient, provided that one uses the appropriate expressions for cluster concentration \( n(\xi) \) and reaction rate \( R(\xi) \). The scaling behavior of these functions near the critical point of a second-order transition was discussed, and a dynamic scaling formula for the nucleation rate derived.

It is crucial to consider the combined effects of nucleation and growth for an interpretation of the experimental enhancement of the accessible undercooling before the transition occurs near the critical point (Fig. 3). For nucleation in fluids far away from \( T_c \), the energy barriers at this metastability limit are of the order of \( F(\xi^*)/k_B T \approx 50 \), and corrections to the classical
theory are hardly important. Due to critical slowing down near \( T_c \) the relevant barrier heights are lower, and corrections become the more important the closer one comes to \( T_c \). The accuracy of the present data does not yet allow an unambiguous assessment of this crossover away from the classical behaviour (Fig. 10), but it is hoped that such data should be available in the near future. Note also that a study of this crossover to low barrier heights is interesting because, then, the density of the critical nuclei strongly increases. Ultimately, one enters a regime of general instability of the system and a broad class of long-wavelength fluctuations (spinodal decomposition) /16/.

The regime of lower barrier heights is relevant, away from \( T_c \), if one considers times for the completion of the phase transitions which are considerably smaller than 1 s, as e.g. in laser-induced nucleation where the time is \( 10^{-9} \) s. It must be noted, however, that present nucleation theories work only for situations very close to thermal equilibrium, where the system reaches its final temperature very quickly in comparison with the time needed to complete the transition. An extension of nucleation theory to systems far away from equilibrium does not seem to be straightforward. Much remains to be done before a satisfactory theory for the kinetics of all kinds of first-order phase transformations is at hand.

References

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