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Monte Carlo Study of the Surface Area of Liquid Droplets

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Computer simulation of droplets containing l molecules ($l \leqslant 1000$) in a lattice gas shows that the average surface area is proportional to $l^{\sigma'}$; $\sigma' \simeq 0.6$ in two and $\sigma' = 0.825$ in three dimensions for small droplets. These exponents agree approximately with those in Kadanoff's modification of Fisher's droplet model near critical points [$\sigma' = (1 + \beta)/\beta\delta$; our T/T_c is 0.4, 0.7, and 0.9]. For larger droplets, these exponents change to 1/2 ($d = 2$) and 2/3 ($d = 3$), the transition occurring for droplet diameters larger than the coherence length and smaller than the critical diameter in the nucleation of supersaturated vapors. This latter result rises some doubts on a recent nucleation theory of Eggington *et al.*

KEY WORDS: Monte Carlo; lattice gas, surface area; surface tension; droplet model; critical point; scaling laws; nucleation.

1. INTRODUCTION

Fisher's liquid droplet model[1] is a semiphenomenological description of critical phenomena which yields the scaling laws [1] and agrees surprisingly well[2] with experiment for gases if $T \leqslant T_c$. Also, it has been applied[3] to calculate the rate at which large droplets are formed in a supersaturated vapor (homogeneous nucleation). In the droplet model, small liquid droplets occur in the gas phase due to thermodynamic fluctuations. One essential ingredient of the model is the surface exponent σ. This is defined in Fisher's model by: (surface free energy) $\propto$ (surface area S_l) $\propto l^{\sigma}$ for a liquid droplet

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Table I. Critical Exponents in the Droplet Model[a]

	Small droplets[b]	Small droplets[c]	Macroscopic droplets
Droplet surface	l^{σ}	$l^{\sigma+(1/\delta)}$	$l^{(d-1)/d}$
Droplet volume	l	$l^{1+(1/\delta)}$	l
Surface tension	l^{0}	$l^{-1/\delta}$	l^{0}
Surface free energy	l^{σ}	l^{σ}	$l^{(d-1)/d}$

[a] Only powers of l, not of $T - T_c$, are shown. $\sigma = 1/\beta\delta$; d = dimensionality.

[b] Fisher's model.

[c] Kadanoff's model.

containing l molecules. This exponent σ is fitted on the measured critical indices (we employ his standard notation(1)) by $\sigma = 1/\beta\delta$ (Table I): in three dimensions, usually $0.6 \leqslant \sigma \leqslant 0.67$. In a modified interpretation proposed by Kadanoff(4) and discussed elsewhere,(5) the density difference between a droplet with l molecules and the surrounding medium is assumed to be not a constant near T_c as in Ref. 1 but to vary as $l^{-1/\delta}$. Then, the droplet volume V_l is proportional to $l^{1/(1+\delta)}$, the droplet surface $S_l \propto l^{\sigma+(1/\delta)}$, with σ still given by $\sigma = 1/\beta\delta$. The surface tension is assumed in this interpretation to be proportional to the density difference and thus proportional to $l^{-1/\delta}$; thus the surface free energy of a droplet is proportional to $S_l l^{-1/\delta} \propto l^{\sigma}$, as in Fisher's interpretation. In Fisher's version, geometric considerations require $\sigma \geqslant 2/3$ in three dimensions ($\sigma = 2/3$ for spherical droplets), a condition violated in the lattice gas (Ising model). Instead, in Kadanoff's picture, the same consideration, that $S_l V_l^{-2/3}$ should not vanish for $l \to \infty$, gives the new relation(5,20) $1 + \beta \geqslant 2\nu$ [$\geqslant (d-1)\nu$ in d dimensions] and

$$1 + \beta = (d-1)\nu \qquad \text{for spherical droplets} \tag{1}$$

The inequality is valid in the lattice gas for $d = 2, 3, 4$, whereas the equality sign does not hold for $d = 2$ and is slightly violated for $d = 3$. In both models, the microscopic surface tension vanishes at T_c, but in general not with the same power of $T_c - T$ as the bulk surface tension.(2,5) It has been unclear where the transition lies between the small droplets (microscopic surface tension) important for the equation of state in the droplet model,(1,2) and the large spherical droplets observable, e.g., as raindrops (bulk surface tension). This question is important for the theory of homogeneous nucleation (see Ref. 6 for a recent review), since most nucleation theories assumed the "critical" droplets to be spherical (large-droplet limit), whereas Eggington *et al.*(3) assumed nonspherical droplets for CO_2 near T_c (small-droplet limit).

Therefore we undertook a Monte Carlo calculation on an IBM 360/91 computer in order to clarify the following questions for a two- and three-dimensional lattice gas: Is the average surface area of a droplet containing l molecules proportional to some power of l, and what, then, is the exponent? Does the result agree better with Fisher's or with Kadanoff's interpretation of the droplet model? Is there a transition between large and small droplets? How does this affect the theory of homogeneous nucleation? In the following section, we describe our mathematical method, in Section 3, its results, and in Section 4, the consequences for theories of the equation of state and of homogeneous nucleation.

2. COMPUTATIONAL TECHNIQUE

The lattice gas(7) is a simple model of a fluid. Each lattice site is either empty or occupied by one molecule. This is the fluid analog to a spin-1/2 Ising model for ferromagnets, the empty sites corresponding to spin down, the occupied sites to spin up. The critical density ρ_c is reached if half of the sites are occupied (zero magnetization); at low temperatures, the density of the liquid phase is therefore $\sim 2\rho_c$. We assume a simple cubic or square lattice in three and two dimensions, respectively, with next-neighbor interaction energy $4J$. Then, the critical temperature T_c is reached(7) at $J/k_B T_c = 0.222$ ($d = 3$) and $J/k_B T_c = 0.441$ ($d = 2$). The total energy is

$$E = \sum_i \sum_k J \cdot s_i s_k$$

with $s_i = +1$ for occupied and $= -1$ for empty sites; in the sum, k runs only over the 4 or 6 next neighbors of sites i. On the computer, we use a finite number of sites up to $20^3 = 8000$ ($d = 3$) or $50^2 = 2500$ ($d = 2$), employing periodic boundary conditions. In the Monte Carlo calculation, suitable configurations of the systems are choosen by using random numbers. Generating a new configuration, the energy difference ΔE between the old and the new configurations is calculated. If $\Delta E < 0$, the new configuration is taken into account in the average; if $\Delta E > 0$, the transition probability $e^{-\Delta E/k_B T}$ is compared with some random number; if the probability is greater, the new configuration is taken into account in the averaging procedure; otherwise, the old configuration is counted once more. By this procedure, configurations are choosen with a thermodynamic probability proportional to $e^{-E/k_B T}$ (see Refs. 8 and 9 for details). In some cases, the number of sites was varied to show that the periodic boundary condition introduces a negligible error only. It has been shown previously(10) that the periodic boundary condition affects the behavior of the system only very near T_c. We have taken into account up to 10^5 configurations (10 min computing time) for a single average in Fig. 1.

If we were to choose the configurations completely at random, we would get a realistic picture of the lattice gas, but not the behavior of large droplets. For, then, most molecules would be arranged in clusters of radius smaller or equal to the coherence length; extremely few droplets with a larger radius would occur. Also, it would be very difficult to uniquely define a droplet and its surface. Thus, instead, we take into account only configurations having a droplet consisting of a given number of molecules (occupied sites). The droplet surface is defined by a sharp double layer. One layer of occupied sites connected by next-neighbor interactions gives the boundary of the liquid region; the adjacent layer of nonoccupied sites is the boundary of the gas phase. Such a sharp boundary is unrealistic very near T_c ; thus we choose $T/T_c \leqslant 0.9$. (Very near T_c , in the interior of the droplet, the density is slightly above ρ_c , in the surrounding gas it is slightly below ρ_c . In between, we expect(11) a smooth transition, whereas in our calculation, this transition region consists of a liquid layer with $\rho = 2\rho_c$, and a gas layer with $\rho = 0$; this is not realistic.) The chemical potential is fixed to be the potential at which bulk gas and bulk liquid can coexist (zero magnetic field); the total number of molecules is not fixed: Outside the droplet, but separated from it, there can be single molecules or small droplets. Also, inside the droplet, small holes occur, enlarging the volume of the droplet (since the number of molecules within the droplet is constant); these internal surfaces are not added to the droplet surface area. The droplet surface area is evaluated by counting for each molecule of the occupied boundary layer of the droplet the number of empty sites which are next neighbors of this molecule; then, these numbers are summed up for all molecules in the boundary layer, the sum being the surface area in units of a^2 (a = lattice constant). Because of the cubic structure of the lattice gas, the energy minimum is reached for a cubic droplet and not a spherical one; a cube of $10^3 = 1000$ closely packed molecules has, by our definition, a surface of $6 \times 10^2 = 600a^2$, as it should be.

We start the Monte Carlo calculation with a cube of molecules (square in two dimensions). The sites in the interior of the cube are labeled with index 1 (initally, all these sites are occupied by molecules, up spins). The molecules at the surface of the cube are labeled with index 2. Their nearest neighbors with down spins have index 3, and the more remote spins outside the droplet have index 4. These indices serve to indicate the local position of the droplet surface, given by the double layer of sites with indices 2 and 3. Now, we select at random two spins to be reversed, in order to get a new configuration of occupation numbers for the sites in our volume. This choice is considered as a trial configuration for our Monte Carlo procedure only if the number of molecules (occupied sites, up spins) within the droplet (indices

1 and 2) remains constant. This is possible if, e.g., we flip a spin of index 2 together with a spin of index 3. Otherwise, a new choice has to be made. If this trial configuration is admitted as a new configuration in the Monte Carlo sequence, we have to correct the values of the surface indices at the positions of the flipped spins and at some of their neighboring positions in such a way that index 1 again corresponds to the droplet interior, index 2 to the connected boundary layer of occupied places, index 3 to the adjacent empty layer, and index 4 to the gas region away from the droplet. Thus the actual position of the boundary layer is given by the surface indices 2 and 3 at any step of our procedure. Repeating these simple steps at arbitrary times, the boundary layer is shifted and bent, but not destroyed, since precautions are taken to avoid separation of the droplet into two parts, etc. While sites of index 2 must be occupied and sites with index 3 must be empty by definition, this is not the case for sites with indices 1 and 4. According to the chosen temperature, there also exist some additional droplets in the gas phase (index 4, but occupied); they are not counted as parts of the droplet. Also in region 1, some bubbles (empty sites within the droplet) are allowed; the lowest density reached in our calculation for three dimensions is $1.84\rho_c$ for region 1 ($T/T_c = 0.9$). One is not allowed to reverse those spins of index 3 that are nearest neighbors to molecules outside the droplet, since the number of molecules in the droplet must be kept constant (if one had allowed these reversals, molecules outside the droplet would by definition have become part of the droplet, and therefore the condition that there be a constant number of molecules within the droplet would have been violated). Essentially, we thus have taken into account for the surface area fluctuations the excluded volume corrections,(1) which means that two droplets cannot be at the same place at the same time.(21)

Since a factor exp(-energy/k_BT) is employed for the probability of each new configuration, at zero temperature, the cube would never change (heavy lines in Fig. 1); the deviations from this behavior (Fig. 1 and 2) are due to the thermal fluctuations we are interested in.

3. RESULTS

Figure 1 gives our results: For two (lower curves) and three (upper curves) dimensions, our points give the mean surface area for various droplet sizes and temperatures. For small droplets, the average surface area S_l is proportional to $l^{0.6}$ in two and to $l^{0.825}$ in three dimensions. These exponents agree much better with Kadanoff's picture $S_l \propto l^{\sigma+(1/\delta)} = l^{0.6}$ ($d = 2$) and $S_l = {}^{0.84\pm0.02}$ ($d = 3$) than with Fisher's picture $S_l \propto l^{\sigma} = l^{0.53}$ ($d = 2$) and $S_l = l^{0.64\pm0.02}$ ($d = 3$). (We have $\sigma = 1/\beta\delta$; $\beta = 1/8$, $\delta = 15$ in two, and $\beta = 0.313 \pm 0.002$, $\delta = 5.0 \pm 0.1$ in three dimensions.(7,12))

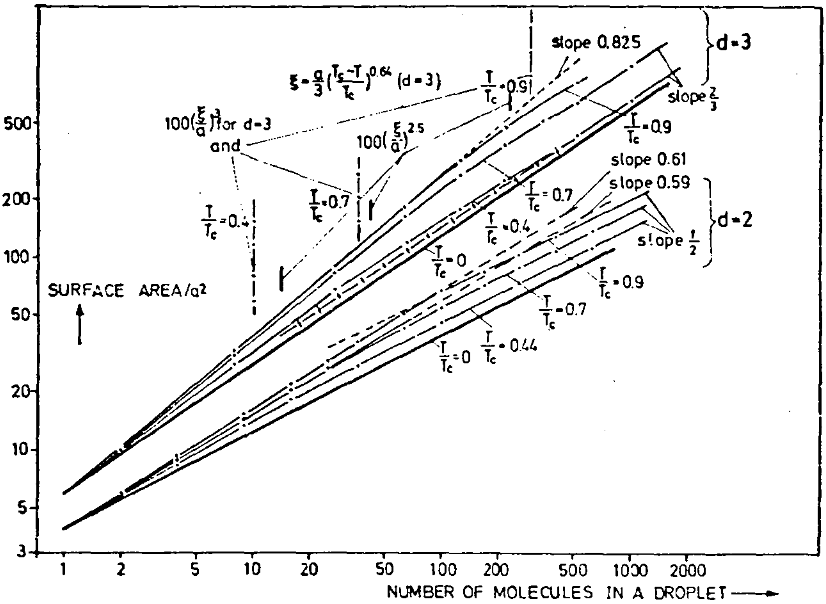

Fig. 1. Average surface area as a function of droplet size. The calculated points are connected by the thin lines.

For larger values of l, a gradual transition occurs to simple $S_l \propto l^{1/2}$ and $S_l \propto l^{2/3}$ laws. Very near T_c, such a transition can be expected from Kadanoff's picture by discussing the density or the surface tension of a small droplet. [For the surface tension argument, we need the "droplet scaling law" (1).]

Density. The density difference between a droplet and the surrounding medium [or $\rho_{\text{droplet}} - \rho_c(\text{near } T_c)$] is proportional to $l^{-1/8}$ very near T_c in Kadanoff's picture. However, our lattice gas has a maximum density $2\rho_c$ (all sites occupied); and since small clusters cannot have holes, only for l greater than some l_1 ($\sim$30 for $d = 3$) can the density difference vary as $l^{-1/8}$. For droplet size l greater than some other boundary l_2, the density within the droplet should be constant again and equal to the density of a bulk liquid at that temperature. Thus we have a transition from a microscopic cluster to a macroscopic raindrop. Very near T_c, where the coherence length ξ is much larger than the lattice constant a {we assume$^{(7)}$ $\xi = (a/3)[1 - (T/T_c)]^{-\nu}$, $\nu = 0.64$}, we have apart from a factor $\sim$1,

$$(\rho_{\text{bulk liquid}} - \rho_c)/\rho_c = (\xi/a)^{-\beta/\nu} \tag{2}$$

[To derive Eq. (2), we expressed$^{(7)}$ the density and the coherence length in powers of $T_c - T$ and then eliminated the temperature.] The density within a droplet varies with size very near T_c roughly as

$$(\rho_{\text{droplet}} - \rho_c)/\rho_c = (l/l_1)^{-1/\delta} \qquad (l_1 \leqslant l \leqslant l_2) \tag{3}$$

Matching both expessions at the boundary $l = l_2$, $\rho_{\text{droplet}} = \rho_{\text{bulk liquid}}$, we find

$$l_2/l_1 = (\xi/a)^{\beta\delta/\nu} = (\xi/a)^{2.5}; \qquad l_2 \sim 30(\xi/a)^{\beta\delta/\nu} \tag{4}$$

The volume of a droplet in Kadanoff's picture(5) is $V_l \propto l^{1+(1/\delta)}$; $V_l = a^3 l^{1+(1/\delta)}/l_1^{1/\delta}$. At the transition $l = l_2$, this volume is therefore

$$V_{l_2} = a^3 l_1 (\xi/a)^{[1+(1/\delta)]\beta\delta/\nu} = a^3 l_1 (\xi/a)^{(2-\alpha)/\nu} = l_1 \xi^3 \sim 30\xi^3 \tag{5}$$

using the scaling law $2 - \alpha = d\nu$ for $d = 3$. In Fig. 1, the transition size seems to be proportional to $(\xi/a)^3$ or $(\xi/a)^{2.5}$ as extrapolated from the critical region. But the factor of proportionality is 100 rather than the 30 to be expected from (4) and (5).

Surface Tension. Another argument leads to a transition size l_3 of the same order of magnitude as the l_2 in (4). The surface free energy(2,5) of small droplets is $k_B T \mid \ln x \mid l^\sigma$; thus the surface tension in Kadanoff's picture equals $k_B T \mid \ln x \mid l^\sigma/S_l = k_B T \mid \ln x \mid l^{-1/\delta} S_l$, with $\ln x \propto T_c - T$ and $S_l = S_1 l^{\sigma+(1/\delta)}$. Whereas this microscopic surface tension vanishes linearly in $T_c - T$ for fixed droplet size l, the bulk surface tension for large droplets(11) is $\gamma = \gamma_0[1 - (T/T_c)]^{2\nu}$ according to the usual scaling laws. Now we assume the additional relation (1) for $d = 3$, which is nearly exact for the three-dimensional lattice gas (3 % error). Then,(5) for droplets of radius proportional to the coherence length, the microscopic surface tension has the same temperature dependence as the bulk one near T_c because now

$$l^{-1/\delta} \propto \mid \ln x \mid^{1/(\sigma\delta)} \propto (T_c - T)^\beta = (T_c - T)^{2\nu-1}$$

Both surface tensions can thus be matched at some

$$l_3 \propto (\xi/a)^{\beta\delta/\nu} \propto (T_c - T)^{-1/\sigma} \propto l_2 :$$

$$\text{Microscopic surface tension near } T_c = (k_B T_c/DS_1)(3\xi/a)^{-(1/\nu)} l^{-(1/\delta)} \tag{6}$$

$$\text{Bulk surface tension near } T_c = \gamma_0[(3\xi/a)^{-1/\nu}]^{2\nu} \tag{7}$$

[In (6), $D = (T - T_c)/T_c| \ln x |$ is a constant.(2) Equations (6) and (7) match at

$$l_3 = (k_B T_c/DS_1\gamma_0)^\delta (3\xi/a)^{\delta[2-(1/\nu)]} = (k_B T_c/DS_1\gamma_0)^\delta\, 3^{\beta\delta/\nu}(\xi/a)^{\beta\delta/\nu} \propto l_2 \quad (8)$$

using $1 + \beta = 2\nu$. If data for Xe or CO_2 are used, l_2 and l_3 are of the same order of magnitude; and both estimates are only order-of-magnitude estimates.

[In two dimensions, very near T_c, Eq. (4) reads $l_2/l_1 = 0.5(\xi/a)^{\beta\delta/\nu}$; $\xi/a = 0.3T_c/(T_c - T)$, whereas no analog of (8) can be found since the droplet scaling law (1) is invalid for $d = 2$ for reasons which are not clear to us; perhaps there exist several transition sizes with different temperature dependences near T_c, and the surface tension might be a nonlinear function of the density difference. No satisfactory solution can be given by us.]

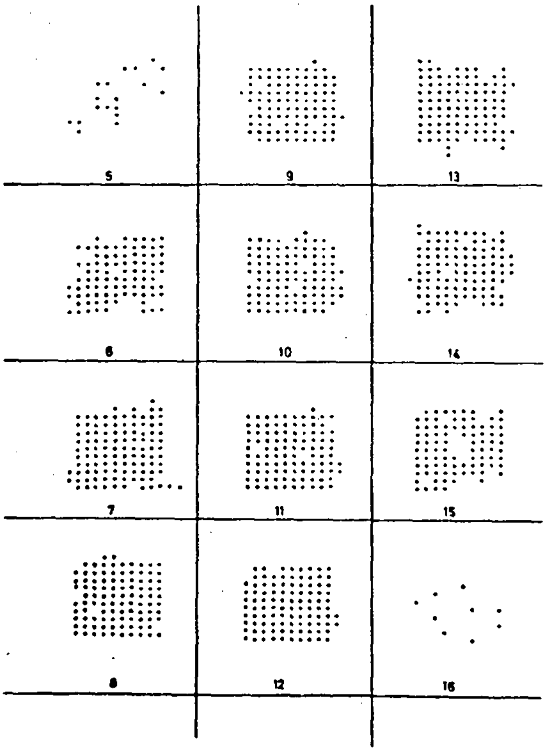

Fig. 2. Typical "critical" droplet for the nucleation in a supersaturated vapor. $T = 0.7T_c$, 10^3 molecules in the droplet, 20^3 sites in the volume. The surrounding volume is not fully shown; also, molecules outside the droplet are not shown. The 12 figures are the adjacent cuts through the lattice planes of the droplet.

Contrary to these two order-of-magnitude estimates of the transition size, the temperature in our Monte Carlo calculation is not very near T_c; thus $\rho_{\text{bulk liquid}}$ is still near $2\rho_c$, and thus, because of their limited accuracy, we cannot study from our results the variation of density with droplet size. Therefore there is no full agreement between our results and Kadanoff's picture. In order to get a clearer picture of the density within a droplet and its variation with size, we need data much nearer to T_c : here, our method of defining a droplet by a sharp double layer of occupied and empty sites would no longer be accurate. From our present data, we guess that the exponents for the average surface area are nearly independent of temperature for both small and large droplets; for small droplets, they agree with Kadanoff's picture: $S_l \propto l^{(1+\beta)/\beta\delta}$; for larger droplets, they are given by $S_l \propto l^{(d-1)/d}$. The transition between large and small droplets is strongly temperature-dependent; it occurs for droplet diameters larger than, but proportional to, the coherence length (for $d = 3$).

For droplets much larger than the transition size, the surface is proportional to $l^{(d-1)/d}$, but the data at $T \sim 0$ do not match the heavy $T = 0$ lines in Fig. 1. For, even a flat surface has a finite roughness[11] (thickness $\sim\xi$). A typical picture is shown in Fig. 2. (Because of the cubic structure of the lattice gas, the typical configuration is still a cube and not a sphere for $d = 3$ at these temperatures; in two dimensions, our largest droplets are more circular.) With our definition of the surface area, the surface roughness is interpreted as an enlargement of the surface area. In the experimentally measured surface tension and surface area, this roughness is already taken into account and need not be added to the surface area; therefore the surface free energy for these very large droplets should be equal to the area of a given sphere (or cube) multiplied by the measured bulk surface tension. The line -|- in Fig. 1 ($d = 3$, $T = 0.4T_c$) is such an extrapolation of the very large droplet behavior ($l = 10^3$) to the intermediate region around 10^2 molecules (extrapolated with slope 2/3). We see that there are small deviations, at least in three dimensions, the actual surface area is larger than the one extrapolated from the bulk behavior.

4. DISCUSSION

We need the droplet surfaces in three dimensions for two purposes: To calculate an equation of state[1,2] of a real gas, particularly near T_c, and to estimate the nucleation rate in a supersaturated vapor.[3,6] In the sums for the equation of state, the important contribution near T_c comes from $l = 1, 2, \ldots$ or $l \sim l_\xi$, where $l_\xi = |\ln x|^{-1/\sigma} \sim (\xi/a)^{2.5}$ is the number of molecules whithin a droplet of size coherence length.[3] For these small droplets, it seems to be safe, according to our data, to assume a simple power law

$S_l \propto l^{\sigma'}$ for the droplet surface. Moreover, our data justify the determination of these exponents from the measured critical indices β and δ from Kadanoff's picture $\sigma' = 1/\beta\delta$, whereas it is dangerous to assume a surface area proportional to $l^{2/3}$ (as in(13–15)).

For the nucleation in supersaturated vapors, however, the important droplet sizes are much larger. If the rate at which macroscopic droplets are formed is about one droplet per sec and cm^3, then(3) we need to know the droplet free energy for $l \sim 10^3 l_\xi$ (critical size, determined by the maximum of the droplet free energy in the supersaturated state; Fig. 2 shows a droplet of roughly critical size at $T = 0.7T_c$). This size is greater than the transition size $l_2 \sim 10^2 l_\xi$ between the large-droplet and the small-droplet behavior; only for very high nucleation rates ($>10^{10}$ cm^{-3} sec^{-1}) or extremely near T_c, the critical size is about the transition size or smaller. Eggington *et al.*(3) calculated $\sigma = 0.635$ from the critical indices β and δ measured in CO_2 and applied this exponent to the nucleation theory near T_c. This procedure now seems to us doubtful; it would probably have been better to use the bulk exponent 2/3 instead of 0.635 in the surface free energy for the critical droplet. Also, one should use for the nucleation theory a bulk surface tension with small curvature corrections (cf. Sarkies and Frankel(16)) instead of a microscopic surface tension determined from the equation of state. The most essential point of Ref. 3, the discussion of the logarithmic term in the droplet free energy and the resulting critical slowing down of the nucleation rate, is essentially unaffected by our present results. (Cf. Stillinger.(15)) (For water in the atmosphere, $T = 0.4T_c$, the bulk surface tension happens to agree with the microscopic droplet surface tension,(3) and the exponent $\sigma = 1/\beta\delta$ is just 2/3; thus the results for water near the triple point probably remain unchanged by our criticism; in fact, they agree with experiment.(3)) It should be noted, however, that we calculated only the surface area and not the surface free energy entering into the nucleation rate, and that the lattice gas is an oversimplified model for a real gas; for example, it gives no vibration frequencies (cf. Ref. 17.)

Concluding, we guess that it is a good approximation to use Fisher's droplet model (with Kadanoff's modification(5)) to evaluate an equation of state; but one should not, contrary to Refs. 3 and 14, extrapolate all parameters for the droplet surface found from the equation of state to the much larger droplets important in the nucleation of supersaturated vapors. A serious drawback of our method, which precludes its application very near T_c, is the sharp double layer used to define the surface. We plan to evaluate in a different manner, but also by Monte Carlo calculations, the smooth surface between bulk liquid and bulk gas, keeping the surface at its desired place by a small gradient in the chemical potential ("gravitational field"). (Cf. Ref. 18 for the liquid–solid interface.) Perhaps then a similar method can also be applied to study droplets very near T_c without the unphysical double layer. A more detailed report on the present computer results is available upon request.⁽¹⁹⁾

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REFERENCES

1. M. E. Fisher, *Physics* **3**:255 (1967).
2. C. S. Kiang, *Phys. Rev. Letters* **24**:47 (1970); C. S. Kiang and D. Stauffer, *Z. Physik* **235**:130 (1970); W. Rathjen, preprint, Munich, 1971.
3. A. Eggington, C. S. Kiang, D. Stauffer, and G. H. Walker, *Phys. Rev. Letters* **26**:820 (1971); C. S. Kiang, D. Stauffer, G. H. Walker, O. P. Puri, J. D. Wise, Jr., and E. M. Patterson, *J. Atmos. Sci.* **28**:1222 (1971).
4. L. P. Kadanoff, Summer School "Enrico Fermi," Lectures, Varenna, 1970.
5. D. Stauffer, C. S. Kiang, and G. H. Walker, *J. Stat. Phys.* **3**:323 (1971); cf. L. Reatto, *Phys. Letters* **33A**:519 (1970) and *Phys. Rev.* **B5**:204 (1972).
6. S. Toschev, Int. Summer School Crystal Growth, Lectures, Leiden, 1971.
7. M. E. Fisher, *Repts. Progr. Phys.* **30**:615 (1967).
8. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**:1087 (1953).
9. J. R. Ehrman, L. D. Fosdick, and D. C. Handscomb, *J. Math. Phys.* **1**:547 (1960).
10. K. Binder and H. Rauch, *Z. Physik* **219**:201 (1969).
11. S. Fisk and B. Widom, *J. Chem. Phys.* **50**:3219 (1969). D. Stauffer, *Z. Physik* **221**:122 (1969).
12. A. J. Guttmann, C. Domb, and P. F. Fox, *J. Physique* (*Suppl.*) **32**:C1-354 (1971).
13. T. Tseng, S. Feng, C. Cheng, and W. Band, *J. Chem. Phys.* **8**:20 (1940).
14. F. F. Abraham, *J. Appl. Phys.* **39**:3287 (1968).
15. F. H. Stillinger, Jr., *J. Chem. Phys.* **39**:3287 (1968).
16. K. W. Sarkies and N. E. Frankel, *J. Chem. Phys.* **54**:433 (1971) and preprint.
17. J. J. Burton, *Chem. Phys. Lett.* **7**:567 (1970); *Surface Sci.* **26**:1 (1971); D. J. McGinty, *J. Chem. Phys.* **55**:580 (1971).
18. P. Bennema and G. H. Gilmer, *Int. Summer School Crystal Growth*, Lectures, and private communication (1971).
19. K. Binder, in preparation.
20. F. P. Buff and R. A. Lovett, in *Simple Dense Fluids*, H. L. Frisch and Z. W. Salsburg, eds. (Academic Press, New York, 1968), p. 22.
21. D. Stauffer and C. S. Kiang, *Phys. Rev. Letters* **27**:1783 (1971).