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Physical Clusters, Surface Tension, and Critical Phenomena

FRANK H. STILLINGER, JR.

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

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A physical-cluster theory of condensation and critical phenomena is developed in which primary emphasis is placed on collective modes of oscillation of clusters under the restoring force of their surface tension. A procedure is advocated for self-consistent inclusion of surface mode interaction leading to a nonlinear integral equation whose solution yields a wavelength-dependent surface tension. An explicit expression is derived for the physical-cluster-size distribution near condensation, and from it follows prediction of critical exponents δ (critical isotherm degree), γ' (initial compressibility below T_c), ν' (correlation length), and η (deviation from Ornstein-Zernike pair distribution at the critical point), in terms of the phenomenological coexistence curve (β) and surface tension (σ) exponents, as well as a parameter ν , which is not directly measurable. The predictions are not consistent with the so-called "scaling laws," except for special ν values that seem experimentally unacceptable. Reasons are listed indicating fundamental differences between the critical phenomena in lattice gases enjoying high current theoretical fashionability, and continuum fluid models. For a range of ν values, the physical cluster theory predictions agree well with experiment. Appendices are devoted to an interfacial fluctuation theorem, and to an outline of the present physical-cluster theory in two dimensions.

I. INTRODUCTION

Although quite a few years have passed since the original formulations of physical-cluster theory were exposed for public scrutiny,¹⁻³ only recently have the implications of this approach for the mathematical structure of condensation^{4,5} and critical phenomena^{6,7} been probed at all deeply. This developmental lag undoubtedly resulted from the pre-eminence accorded the alternative and more elegant Ursell-Mayer cluster theory^{8,9} during the intervening period. However, the physical cluster theory may be placed on as systematic a basis as its rival, and it has as well the virtue that its

quantitative pronouncements are directly amenable to intuitive physical understanding. In the very difficult field of critical phenomena, this latter aspect provides especially valuable guides.

It is our intention here to pursue several aspects of the physical cluster theory relevant to the liquid-vapor condensation process in simple real fluids, such as the noble gases, as well as other substances with small, nearly spherical, nonpolar molecules (N_2 , CH_4 , SF_6 , etc.). We utilize throughout the techniques of Gibbsian classical statistical mechanics, so that it is necessary to exclude from consideration helium and molecular hydrogen, for which quantum-mechanical effects are important.

In the analysis below considerable emphasis is placed on the surface free energy of the roughly globular clusters, and on the surface wave cluster oscillations for which it provides the restoring force. Such droplet oscillations have been considered before in connection with estimation of capture cross sections in nucleation kinetics.¹⁰ The particular application in this paper is new, however, and the specific scheme for self-consistent inclusion of surface mode interaction is to the author's knowledge advocated here for the first time.

¹⁰ R. A. Lovett, "Statistical Mechanical Theories of Fluid Interfaces," doctoral dissertation, University of Rochester (1965).

¹ J. Frenkel, *J. Chem. Phys.* **7**, 200, 538 (1939).

² W. Band, *J. Chem. Phys.* **7**, 324, 927 (1939).

³ A. Bijl, "Discontinuities in the Energy and Specific Heat," doctoral dissertation, Leiden (1938).

⁴ A. F. Andreev, *Soviet Phys.—JETP* **18**, 1415 (1964) [*Zh. Eksperim. i Teor. Fiz.* **45**, 2064 (1964)].

⁵ J. S. Langer, *Ann. Phys. (N. Y.)* **41**, 108 (1967).

⁶ J. W. Essam and M. E. Fisher, *J. Chem. Phys.* **38**, 802 (1963).

⁷ M. E. Fisher, "The Theory of Condensation," in the *Proceedings of the Centennial Conference on Phase Transformation*, University of Kentucky, 1965; *Physics* (to be published). This chapter comprises a convenient review, with relevant literature references, of most of the mathematical aspects of the cluster theory of condensation.

⁸ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chaps. 13 and 14.

⁹ G. E. Uhlenbeck and G. W. Ford, in *Studies in Statistical Mechanics* (North-Holland Publ. Co., Amsterdam, 1962), Pt. B, Vol. I.

The natural starting point is provided by the formally exact relation between distribution of molecules among clusters in an open system at equilibrium, and chemical potential μ that was derived in our earlier investigation¹¹ of the rigorous basis of physical cluster theory. In a vessel of volume V , the mean member of molecules N may first be regarded as composed of subsets belonging to clusters of $s=1, 2, \dots$, molecules present in average

number N_s :

$$N(T, \mu) = \sum_{s=1}^{\infty} s N_s(T, \mu). \quad (1)$$

Then the mean cluster numbers N_s may be found in principle by computing suitable cluster partition functions $Z_s(T, \mu)$:

$$N_s(T, \mu) = \exp(s\mu/kT) Z_s(T, \mu); \quad (2)$$

$$Z_s(T, \mu) = h^{-3s} (s!)^{-1} \int_{(\text{conn})} \cdots \int \exp \left\{ - (kT)^{-1} \left[\sum_{i=1}^s \frac{p_i^2}{2m_0} + V_s(\mathbf{r}_1 \cdots \mathbf{r}_s) + W_s(\mathbf{r}_1 \cdots \mathbf{r}_s; T, \mu) \right] \right\} d\mathbf{r}_1 \cdots d\mathbf{r}_s d\mathbf{p}_1 \cdots d\mathbf{p}_s. \quad (3)$$

V_s is the interaction energy when the s particles forming the cluster are at $\mathbf{r}_1 \cdots \mathbf{r}_s$, and $\mathbf{p}_1 \cdots \mathbf{p}_s$ are the respective momenta. The configuration integrals in Eq. (3) are restricted by the condition that the volumes interior to spheres of diameter b drawn about the centers of all s particles overlap to produce a *connected* region. W_s contains the entire effect of cluster interference; it equals the reversible work required at T, μ to empty a cavity of all other particles so as to accommodate the s cluster's b -sphere envelope.

Although b is nominally arbitrary in definition of cluster-forming particle overlaps, we adopt in the following a particularly convenient choice mentioned in Ref. 11, which follows from the demand that the thermodynamic critical point lie on a certain critical percolation process locus. The resulting unique b value, comparable in range to intermolecular forces, permits identification of the condensation phenomenon as change in mean cluster size on a per-particle basis,

$$\xi(T, \mu) = \left[\sum_{s=1}^{\infty} s^2 N_s(T, \mu) \right] / \left[\sum_{s=1}^{\infty} s N_s(T, \mu) \right], \quad (4)$$

from order-one magnitude to order- V magnitude at all temperatures below the critical temperature T_c .

Before embarking on the detailed asymptotic evaluation of Z_s required for understanding of critical phenomena we dispose of several preliminary matters in the next two sections. Section II reports some general observations and relations in the theory which not only serve to introduce our particular Z_s computation scheme, but may also be useful in future work in the field. Section III contains a rough calculation of physical cluster free energy based upon the van der Waals-Cahn-Hilliard inhomogeneous-fluid theory which is not in itself sufficiently powerful to give Z_s to the requisite precision for analysis of critical phenomena, but which nevertheless serves to justify later important simplifications equivalent to neglect of surface free-energy curvature dependence.

Our central Z_s calculation begins in earnest in Sec. IV,

with a canonical transformation to isolate the surface-wave collective variables. It is pointed out that for large clusters, the principal manifestation of the excluded volume effects in the W_s , so far as the collective variables are concerned, is a renormalization of the surface tension tending to produce spherical clusters. The large- s collective coordinate oscillator frequencies are then identified with the known hydrodynamic oscillation frequencies of a spherical incompressible droplet with surface tension.

Although these cluster oscillations may properly be regarded as independent at low temperature (i.e., just above the thermodynamic triple point), the same is scarcely true near T_c . Thus a self-consistent approach is developed in Sec. V for incorporation of interference between the droplet surface modes, which automatically decouples them at low temperature. The result constitutes use of separate surface tensions for surface modes of separate wavelength (that is, surface tension displays dispersion), with infinite wavelength corresponding precisely to the experimental surface tension in the absence of external gravitational fields.^{10,12}

Section VI proceeds to establish the large- s asymptotic behavior of Z_s along the condensation curve. It is demonstrated that the nonlinear surface tension self-consistency requirement produces a discontinuous change in functional form for the asymptote at T_c , compared with lower temperature.

The problem of predicting critical-region exponents from Z_s is taken up in Sec. VII. It is presumed that the phenomenological exponents β (for the coexistence curve shape) and σ (for surface tension) are known. Then after introduction of hypothetical but plausible interpolation functions for cluster bulk and surface free energy in the critical region homogeneous in $\Delta T = T_c - T$ and $\Delta \mu = \mu$ (condensation, T) $-\mu$, expressions are produced for the critical isotherm degree (δ) and low-temperature initial compressibility index (γ') in terms of β, σ , and a third parameter ν . Although ν cannot be deduced in the present analysis, it may be

¹¹ F. H. Stillinger, Jr., J. Chem. Phys. **38**, 1486 (1963).

¹² F. P. Buff, R. A. Lovett, and F. H. Stillinger, Jr., Phys. Rev. Letters **15**, 621 (1965).

assigned a numerical value which simultaneously fits experimental δ and γ' values for real three-dimensional fluids. The physical cluster theory is also applied in Sec. VII to the pair-correlation function, with the result that the low-temperature correlation range index ν' is identified as $\frac{1}{2}\sigma$ (confirming a result obtained by Widom¹³ previously). Also, the pair-correlation index η (measuring deviation from the Ornstein-Zernike theory at T_c) then follows from the γ' and ν' predictions, and is numerically very acceptable.

The discussion in final Sec. VIII first points out that the exponent predictions obtained here fail to satisfy the currently fashionable "scaling laws"^{14,15} for experimentally acceptable ν values. It is then remarked that lattice-gas models of condensation (which may well obey scaling laws in both two and three dimensions) probably exhibit analytically different critical-point singularities from continuum fluids because of the fundamentally different character of surface free energy.

Two appendices are included. The first is devoted to a surface-fluctuation theorem closely connected with the surface tension self-consistency considerations in Sec. V. The second outlines application of the theory in the paper's main text to continuum fluids in two dimensions.

Although the material in Sec. II and III constitutes an essential ingredient in the over-all logical development of the physical-cluster theory, its character is somewhat supportive to the primary specific argument of this paper. For this reason the reader may find it useful to skip to the beginning of Sec. IV.

II. SOME GENERAL CONSIDERATIONS

The normalized configurational probability for a single s cluster, corresponding to Eqs. (1), (2), and (3), is the following:

$$P^{(s)}(\mathbf{r}_1 \cdots \mathbf{r}_s) = (\lambda^{3s} s! N_s)^{-1} \times \exp\{[s\mu - V_s(\mathbf{r}_1 \cdots \mathbf{r}_s) - W_s(\mathbf{r}_1 \cdots \mathbf{r}_s; T, \mu)]/kT\},$$

$$\lambda = h/(2\pi m_0 kT)^{1/2} \tag{5}$$

defined only for valid cluster-forming configurations. Unless s is so large that the cluster fills a significant fraction of the vessel volume V , $P^{(s)}$ will reflect invariance with respect to translation of the cluster center of mass. In order to study nontrivial average properties of clusters it is therefore convenient to remove center-of-mass motion by a transformation of

variables to barycentric coordinates:

$$\begin{aligned} \mathbf{r}_1' &= (\mathbf{r}_1 + \cdots + \mathbf{r}_s)/s, \\ \mathbf{r}_2' &= \mathbf{r}_2 - \mathbf{r}_1', \\ &\vdots \\ \mathbf{r}_s' &= \mathbf{r}_s - \mathbf{r}_1'. \end{aligned} \tag{6}$$

One finds for the transformation Jacobian

$$\partial(\mathbf{r}_1 \cdots \mathbf{r}_s)/\partial(\mathbf{r}_1' \cdots \mathbf{r}_s') = s^3. \tag{7}$$

By means of the inverse transformation

$$\begin{aligned} \mathbf{r}_1 &= \mathbf{r}_1' + \mathbf{r}_2' + \mathbf{r}_3' + \cdots + \mathbf{r}_s', \\ \mathbf{r}_2 &= \mathbf{r}_2' + \mathbf{r}_1', \\ &\vdots \\ \mathbf{r}_s &= \mathbf{r}_s' + \mathbf{r}_1', \end{aligned} \tag{8}$$

the configurational probabilities may be expressed as functions of the new coordinates. Since \mathbf{r}_1' is nothing but the center-of-mass position (of which the probability is independent for s not macroscopically large), the transformed probability may be written simply as $P^{(s)}(\mathbf{r}_2' \cdots \mathbf{r}_s')$. We can subsequently impose the normalization

$$1 = \int_{(\text{conn})} \cdots \int \hat{P}^{(s)}(\mathbf{r}_2' \cdots \mathbf{r}_s') d\mathbf{r}_2' \cdots d\mathbf{r}_s'; \tag{9}$$

as before, the integration spans only those particle configurations leading to b -sphere cluster connectivity in the original space of $\mathbf{r}_1 \cdots \mathbf{r}_s$.

A direct measure of the average matter distribution in an s cluster may immediately be obtained from $\hat{P}^{(s)}$. Since all s particles are equivalent, the function

$$h_s(\mathbf{r}) = \int_{(\text{conn})} \cdots \int \delta(\mathbf{r}_2' - \mathbf{r}) \hat{P}^{(s)}(\mathbf{r}_2' \cdots \mathbf{r}_s') d\mathbf{r}_2' \cdots d\mathbf{r}_s' \tag{10}$$

is proportional to the matter density of the cluster at position \mathbf{r} relative to the center of mass. Obviously

$$1 = \int h_s(\mathbf{r}) d\mathbf{r}. \tag{11}$$

If the temperature is only slightly above the thermodynamic triple-point temperature, and if s is larger than 10^2 , say, one can reasonably expect the physical cluster to resemble closely a liquid droplet. In other words, it should remain compact and nearly spherical. Then h_s would depend only on the magnitude of \mathbf{r} , and should equal a constant value essentially within the droplet, and fall relatively rapidly to zero beyond the mean surface radial position. This mean radius may be

¹³ B. Widom, J. Chem. Phys. **43**, 3892 (1965), Eq. (14).
¹⁴ B. Widom, J. Chem. Phys. **43**, 3898 (1965).
¹⁵ L. P. Kadanoff, Physics **2**, 263 (1966); also L. P. Kadanoff, D. Aspnes, W. Götze, D. Hamblen, R. Hecht, J. Kane, E. Lewis, V. Palciauskas, M. Rayl, and J. Swift, Rev. Mod. Phys. **39**, 395 (1967).

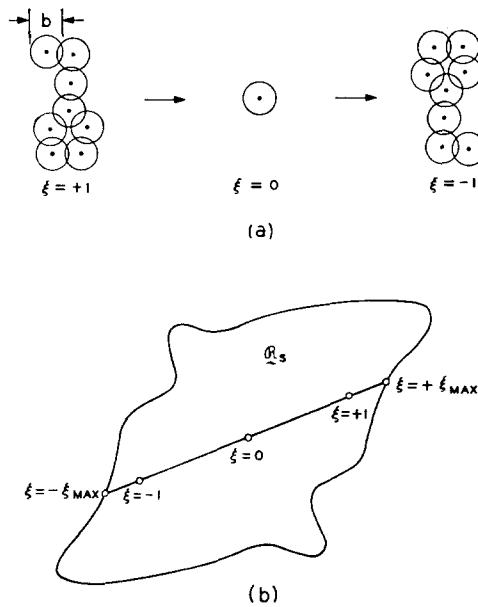


FIG. 1. Schematic diagram of the process shown in Eq. (14). (a) exhibits the uniform cluster contraction and inversion through the center of mass as ξ diminishes from $+1$ to -1 . In (b), the corresponding point in star-shaped region \mathcal{R}_s of the $3(s-1)$ -dimensional configuration space traces a straight line segment contained entirely within \mathcal{R}_s .

obtained from $h_s(r)$ by computing moments of r ,

$$\langle r^n \rangle_s = \int_0^\infty r^n h_s(r) (4\pi r^2) dr, \quad (12)$$

and comparing with the result for a perfect sphere (i.e., a step-function density h_s). In this low-temperature liquid-droplet regime, the moments $\langle r^n \rangle_s$ are surely asymptotically proportional to $s^{n/3}$, for large s .

One of the central features in this paper is the manner in which thermally induced fluctuations destroy the compactness and sphericity of the clusters as temperature increases toward T_c . A measure of the mean-square fluctuation in radial position of the droplet surface is provided by the following combination of moments which vanish identically for a step-function h_s :

$$15 \langle r^2 \rangle_s - 16 \langle r \rangle_s^2. \quad (13)$$

One of the results of examining droplet surface modes as we do in the following section, is the conclusion that this quantity should be asymptotically proportional to $\ln s$ for large s .¹⁰

The connectivity requirement for the cluster we have seen limits the integrals in Eqs. (9) and (10), for instance, to a specific region in the full $3(s-1)$ -dimensional space of $\mathbf{r}_2' \cdots \mathbf{r}_s'$, whose properties we now examine. Let \mathcal{R}_s denote this closed region. Obviously the point $0: \mathbf{r}_2' = \mathbf{r}_3' = \cdots = \mathbf{r}_s' = 0$ lies within \mathcal{R}_s . Let

$\mathbf{r}_2^* \cdots \mathbf{r}_s^*$ be some other point P^* in \mathcal{R}_s ; then setting

$$\begin{aligned} \mathbf{r}_2' &= \xi \mathbf{r}_2^*, \\ &\vdots \\ \mathbf{r}_s' &= \xi \mathbf{r}_s^*, \end{aligned} \quad (14)$$

we see that the effect on the cluster in the P^* configuration of reducing ξ continuously below $+1$ is to shrink the physical cluster uniformly (that is, without shape change) toward its center of mass. Certainly the b spheres continue to overlap for all $0 \leq \xi \leq +1$. The image point in \mathcal{R}_s as ξ runs over this interval is a straight line connecting 0 to P^* , and it lies entirely within \mathcal{R}_s .

Changing the sign of ξ in (14) has the effect of inverting the cluster through its center of mass. Accordingly, the extended line segment $-1 \leq \xi \leq +1$ also lies entirely within \mathcal{R}_s . Actually one can expect to expand this segment symmetrically even further (the precise amount depending on the initial choice of $\mathbf{r}_2^* \cdots \mathbf{r}_s^*$) to include all $-\xi_{\max} \leq \xi \leq +\xi_{\max}$ within \mathcal{R}_s , the endpoints now lying on \mathcal{R}_s 's boundary hypersurface. Since this procedure connects the image point in \mathcal{R}_s for any cluster configuration to 0 by a straight-line segment entirely within \mathcal{R}_s , we conclude not only that \mathcal{R}_s is simply connected,¹⁶ but that it is star-shaped with 0 a center of inversion symmetry. Figure 1 provides a rough illustration.

However we can easily establish, at least for s larger than 4, that \mathcal{R}_s is definitely not convex. Consider the class of configurations shown in Fig. 2, for which the cluster particles are strung out roughly into the shape of the letter "U." The two end particles may be moved symmetrically toward one another along the initial line of centers without disturbing the cluster's center of mass, and eventually they will end up in each other's original positions. The image point for this process then traces out a straight line segment in the configu-

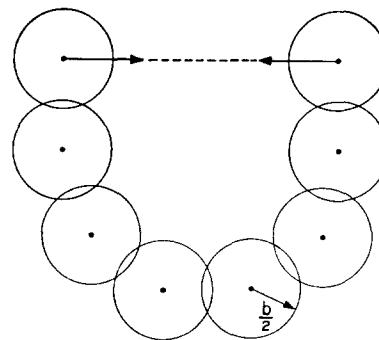


FIG. 2. U-shaped cluster configuration employed in proving that \mathcal{R}_s is nonconvex. In order that the end particles necessarily disconnect from the remainder during their symmetrical linear exchange, there must be a total of four or more particles.

¹⁶ Although the b -sphere domain in ordinary space need not be!

ration space of $\mathbf{r}_2' \cdots \mathbf{r}_s'$, both ends of which lie in \mathcal{R}_s . But it is clear that if $s \geq 4$ the cluster can become disconnected at an intermediate stage of the exchange, so the center of the line segment in configuration space will fall *outside* \mathcal{R}_s . This feature of course indicates nonconvexity.

The transformation (6) is not the only linear transformation which isolates the center of mass. Another choice would be Helmert's orthogonal transformation.¹⁷ Any pair of such coordinate systems are themselves related by a linear transformation, under which the properties deduced for \mathcal{R}_s remain invariant.

As a final matter in this section, we note that cluster configurations, and hence \mathcal{R}_s , may be divided into classes in such a way as to establish a connection with the general theory of polymer statistics with excluded volume. The physical cluster connectivity condition is equivalent to the condition that between any pair of particles in set $1 \cdots s$ there exists a path of straight-line segments connecting particle centers in the set, with each center-center segment length less than or equal to b . For given $\mathbf{r}_1 \cdots \mathbf{r}_s$, let $d_1 \cdots d_M$ denote all distances between pairs of centers less than or equal to b . Of course not only the magnitudes of these distances, but their number M will depend on the cluster configuration, but in any event connectivity obviously requires $M \geq s-1$. We may disregard that zero-measure set of configurations for which any pair of the d_i 's are accidentally equal. Then without loss of generality it may be presumed that the d_i form on ascending sequence

$$d_1 < d_2 < \cdots < d_{M-1} < d_M \leq b. \quad (15)$$

One may imagine that the d_i 's comprise a sort of "framework," which for typical cluster configurations will be highly crosslinked. However, there is an obvious unique prescription for selecting a subset E of the d_i 's which still connects all particle centers, but has no closed polygons within it. This subset thus may be regarded as the backbone of a sort of branched "polymer" or, in the language of the theory of graphs, a Cayley tree.⁹ Set

$$e_1 = d_1, \quad e_2 = d_2, \quad (16)$$

then for the third member e_3 of the desired subset choose d_3 *unless* d_1, d_2 , and d_3 form a triangle, in which

$$Z_s(T, \mu) = \sum_{[E]} h^{-3s} [\tau(E)]^{-1} \int_{(E)} \cdots \int \exp \left\{ - (kT)^{-1} \left[\sum_{i=1}^s \frac{\hat{p}_i^2}{2m_0} + V_s(\mathbf{r}_1 \cdots \mathbf{r}_s) + \Phi(\mathbf{r}_1 \cdots \mathbf{r}_s | E) + W_s(\mathbf{r}_1 \cdots \mathbf{r}_s; T, \mu) \right] \right\} d\mathbf{r}_1 \cdots d\mathbf{p}_s. \quad (19)$$

Here, symmetry number $\tau(E)$ is defined by the requirement that $s!/\tau(E)$ be the number of distinguishable ways of labeling 1 to s the vertices of structure E .

¹⁷ M. G. Kendall, *A Course in the Geometry of n Dimensions* (Hafner Publishing Co., New York, 1961), p. 12.

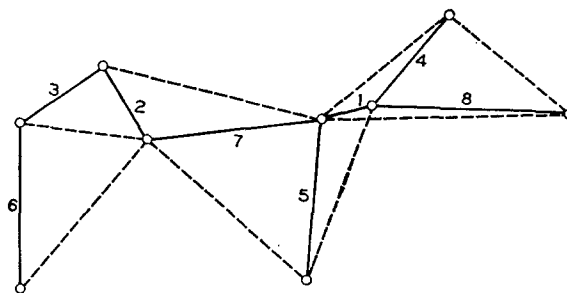


FIG. 3. Distances $d_i \leq b$ drawn between particle centers in a cluster of nine particles. The solid lines are the distances e_j , numbered according to ascending length (i.e., by their order of selection upon use of the algorithm cited in the text).

case choose $e_3 = d_4$. Generally, with

$$e_{n-1} = d_m, \quad M > m \geq n-1, \quad (17)$$

the choice for e_n is then to be the smallest d_i , $M \geq i > m$ which forms no closed polygons with any of the e_j 's already chosen. Figure 3 illustrates this selection procedure, which will automatically terminate with e_{s-1} .

Let us suppose that the particles are restricted just to those configurations $\mathbf{r}_1 \cdots \mathbf{r}_s$ which induce some given backbone structure of linkages e_i between the particles regarded as distinguishable. No two "monomer" particles, which have no direct e_i between them, can be permitted to approach one another more closely than the largest of the e_i bonds (e_l , say) along the unique indirect backbone path between them, for this would have implied that that direct distance would have been in the e set instead of e_l . This requirement of avoidance constitutes a special sort of excluded volume between "monomers," and indeed it may conveniently be expressed in terms of a potential-energy function $\Phi(\mathbf{r}_1 \cdots \mathbf{r}_s | E)$, for any backbone structure. Simply stated,

$$\begin{aligned} \Phi(\mathbf{r}_1 \cdots \mathbf{r}_s | E) &= 0 && \text{if } \mathbf{r}_1 \cdots \mathbf{r}_s \text{ consistent with } E, \\ &= \infty && \text{if } \mathbf{r}_1 \cdots \mathbf{r}_s \text{ inconsistent with } E. \end{aligned} \quad (18)$$

Finally, this singular excluded volume potential function may be incorporated into the cluster partition function in Eq. (3), by summing over all possible unlabeled backbones:

Although this formally exact equivalence between the physical cluster problem and a special polymer excluded-volume problem yields no particularly valuable insights at low temperatures where the clusters are compact and essentially spherical, the contrary

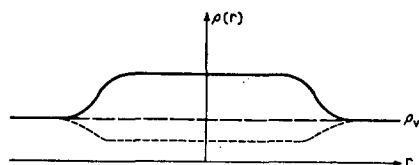


FIG. 4. Total mean density through a physical cluster immersed in vapor with density ρ_v . The cluster's centroid is fixed at $r=0$. Though the broken line represents the constant ρ_v at all r , the density of vapor included as bubbles within the cluster is smaller as exhibited by the dashed curve, which follows from Eq. (24).

may well prove to be true at high temperature. There, it is no longer attractive forces which hold the cluster together, but just the connectivity requirement alone. Clusters presumably will have evaporated out of the compact droplet into very extended spongy entities,¹¹ with radial cluster density $h_s(r)$ and moments $\langle r^n \rangle_s$, undergoing corresponding qualitative changes. It is attractive to speculate that variants of the recently emerging mathematical techniques that Edwards¹⁸ has successfully applied to polymer excluded-volume problems will eventually describe high-temperature physical-cluster behavior.

III. CRUDE CLUSTER PROFILE CALCULATION

It is our purpose now to provide a preliminary assessment of the free energy and density distribution for a cluster with fixed center of mass, while it is actually immersed in the remainder of the fluid system (assumed to be in the vapor state at the condensation curve). Below T_c , the mean particle density along a ray through the fixed cluster's center would appear essentially as shown in Fig. 4; out to the droplet radius the density $\rho(r)$ would approximately be the liquid density then, after a rapid monotonic decline, the constant vapor density ρ_v obtains.

For T well below T_c , the cluster compactness implies that virtually all material inside the interfacial zone shown in Fig. 4 in fact belongs to the cluster. But as T increases toward T_c , bubbles of vapor will be found with increasing frequency encased within the cluster of interest. Since these vapor molecules will not be connected by b spheres to the cluster, we see that a smaller and smaller fraction of the interior density can actually be imputed to the cluster.

Near T_c it is possible to make a rough estimate of this effect. Let ρ^* denote the high density of particle centers occurring in compact, low-temperature clusters. An included bubble at higher temperature falls outside the connected total interior of all s -cluster b spheres (call it $I_b^{(s)}$), so we presume that

$$\rho^* \cong s/I_b^{(s)}, \quad (20)$$

regardless of the size and concentration of bubbles. If $\zeta(r)$ stands for the mean volume fraction of $I_b^{(s)}$ at radial distance r from cluster centroid, then

$$sh_s(r) = \zeta(r)\rho^* \quad (21)$$

¹⁸ S. F. Edwards, Proc. Phys. Soc. (London) **85**, 613 (1965); **88**, 265 (1966).

gives the actual density of particles belonging to the cluster. The function $\rho(r)$ comprises two parts; they are respectively $sh_s(r)$, and the vapor of density ρ_v occupying the remaining volume fraction $1-\zeta(r)$:

$$\rho(r) = \zeta(r)\rho^* + [1-\zeta(r)]\rho_v. \quad (22)$$

Therefore $\zeta(r)$ is the following:

$$\zeta(r) = [\rho(r) - \rho_v]/(\rho^* - \rho_v), \quad (23)$$

so from Eq. (21) we have

$$s = \int sh_s(r) dr = \frac{\rho^*}{\rho^* - \rho_v} \int [\rho(r) - \rho_v] dr. \quad (24)$$

The factor preceding the integral in the last member always exceeds unity, and in the critical region where ρ_v is approximately the critical density ρ_c , it might reasonably be taken as about two. Figure 4 shows pictorially how this enhancement factor divides interior material between cluster and included vapor.

The Cahn-Hilliard¹⁹ variational principal for finding the density distribution in inhomogeneous fluids affords now a convenient descriptive approach from which we deduce a rough density profile $\rho(r)$. It suffices to approximate $\rho(r)$ by a trapezoidal shape, as shown in Fig. 5, with constant interior density ρ_i out to a linear transition zone between r_1 and r_2 :

$$\begin{aligned} \rho(r) &= \rho_i & (0 \leq r \leq r_1), \\ &= \rho_v + (\rho_i - \rho_v)(r_2 - r)/(r_2 - r_1) & (r_1 \leq r \leq r_2), \\ &= \rho_v & (r_2 \leq r). \end{aligned} \quad (25)$$

Although each of ρ_i , r_1 , and r_2 are variable, for given s they are connected by a constraint fixing the number of particles in the cluster:

$$s/\lambda = \frac{1}{3}\pi(\rho_i - \rho_v)(r_1^3 + r_1^2 r_2 + r_1 r_2^2 + r_2^3); \quad (26)$$

here λ is the enhancement factor just discussed which we assume can be taken in leading order as the constant

$$\lambda = \rho^*/(\rho^* - \rho_v). \quad (27)$$

The central idea of the Cahn-Hilliard approach consists in minimizing a functional for the Helmholtz free energy F with respect to all possible density variations at fixed volume and total number of particles:

$$F[\rho] = \int \{ f[\rho(r)] + \frac{1}{2}B[\nabla\rho(r)]^2 \} dr. \quad (28)$$

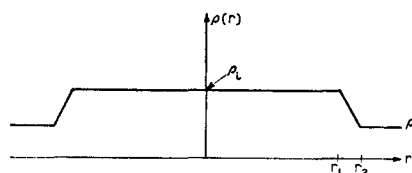


FIG. 5. Trapezoidal density profile utilized in the crude variational calculation of Sec. III.

¹⁹ J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).

f is the homogeneous-fluid Helmholtz free energy per unit volume at density ρ , and the positive coefficient B for the squared-gradient term in Eq. (28) may, for our purposes, be treated as independent of density. In view of the simple trapezoidal-shape assumption, and Condition (26), we employ Eq. (28) variationally only to determine two scalar parameters, rather than an entire function $\rho(r)$.

In that part of the critical region just below T_c , we use a simple approximate free-energy density which is designed to reproduce the experimental nonclassical coexistence curve and compressibility:

$$f(\rho, T) \cong f_0(T) + f_1(\rho - \rho_c) - f_2(T_c - T)^{\gamma'}(\rho - \rho_c)^2 + f_4(T_c - T)^{\gamma' - 2\beta}(\rho - \rho_c)^4, \quad (29)$$

by means of a simple extension (involving fractional exponents γ' and $\gamma' - 2\beta$) of the multinomial development traditionally invoked for classical critical point analysis.²⁰ We leave the temperature dependence of $f_0(T)$ unspecified, but f_1 , f_2 , and f_4 are positive constants.²¹ Coexistent liquid and vapor densities are located by the Maxwell double tangent construction²² carried out on a plot of $f(\rho)$ vs ρ , or equally well $f(\rho)/\rho$ vs $1/\rho$. The coexisting liquid and vapor phase densities are thus found to be:

$$\begin{aligned} \rho_l &= \rho_c + (f_2/2f_4)^{1/2}(T_c - T)^\beta, \\ \rho_v &= \rho_c - (f_2/2f_4)^{1/2}(T_c - T)^\beta, \end{aligned} \quad (30)$$

thereby justifying use of the conventional coexistence index symbol β in (29). Likewise, since

$$\partial p / \partial \rho = \rho(\partial \mu / \partial \rho) = \rho(\partial^2 f / \partial \rho^2), \quad (31)$$

index γ' may be identified as the one appropriate to the initial compressibility at coexistence,

$$\partial p / \partial \rho |_{\rho_v} \propto (T_c - T)^{\gamma'}. \quad (32)$$

For notational simplicity let

$$\begin{aligned} r_1 &= R - \bar{l}, \\ r_2 &= R + \bar{l}, \end{aligned} \quad (33)$$

so that the restraint condition (26) may be written

$$\rho_i = \rho_v + 3s/4\pi\lambda R(R^2 + \bar{l}^2). \quad (34)$$

We are required to minimize $\Delta F(R, \bar{l})$, the difference in free energy between the system with and without the trapezoidal inhomogeneity, with respect to independent variables R and \bar{l} . By using Eq. (34) to

eliminate ρ_i , we find

$$\begin{aligned} \Delta F(R, \bar{l}) &= \int \{ f(\rho) - f(\rho_v) + (B/2)[\nabla \rho]^2 \} dx \\ &= \frac{4\pi}{3}(R - \bar{l})^3 \left[f\left(\rho_v + \frac{3s}{4\pi\lambda(R^2 + \bar{l}^2 R)}\right) - f(\rho_v) \right] \\ &\quad + \frac{3Bs^2(3R^2 + \bar{l}^2)}{16\pi\lambda^2\bar{l}(R^2 + \bar{l}^2 R)^2} + 4\pi R^2 \int_{-1}^{+1} \left(1 + \frac{x}{R}\right)^2 \\ &\quad \times \left\{ f\left[\rho_v + \frac{3s(\bar{l} - x)}{8\pi\lambda\bar{l}(R^2 + \bar{l}^2 R)}\right] - f(\rho_v) \right\} dx. \end{aligned} \quad (35)$$

We can still recognize these three terms in the last member, respectively, as the free energy of the droplet interior, the surface-zone gradient free energy, and the "unnatural density" (i.e., not ρ_l or ρ_v) free energy of the surface zone.

The complete variational expression is too complicated to permit a closed form minimization, but it is well suited for asymptotic expansion of droplet free energy for large s , which is our main objective. We proceed iteratively. At the least accurate level of computation, appropriate in the limit of large s (and hence large R at the ΔF minimum), only the first ΔF term in Eq. (35) needs to be considered, with \bar{l} disregarded:

$$\Delta F \sim \frac{4\pi R^3}{3} \left[f\left(\rho_v + \frac{3s}{4\pi\lambda R^2}\right) - f(\rho_v) \right]. \quad (36)$$

At this first level of approximation the free energy of the interfacial zone, and thus also any appearance of its width $2\bar{l}$, are totally suppressed. Then minimization of Expression (36) with respect to R leads to the condition

$$\begin{aligned} 0 &= f\left(\rho_v + \frac{s}{\lambda v}\right) - f(\rho_v) - \frac{s}{\lambda v} f'\left(\rho_v + \frac{s}{\lambda v}\right), \\ v &= \frac{4}{3}(\pi R^3). \end{aligned} \quad (37)$$

This is merely an algebraic statement of Maxwell's double-tangent construction, so we can immediately infer that the minimum occurs for that R which gives droplet volume v consistent with ρ_i equal just to the equilibrium liquid density ρ_l shown in Eq. (30). This is the inevitable result of course, since the interior and exterior of the droplet are treated at this approximation level merely as distinct bulk phases. From Eq. (34) we have at the ΔF minimum

$$R \cong [3s/4\pi\lambda(\rho_l - \rho_v)]^{1/3} = R_\infty (s/\lambda)^{1/3} \quad (38)$$

upon neglect of \bar{l} again relative to quantities retained. By combining Eqs. (36) and (38), we find the corresponding free-energy estimate for the droplet to be

$$\Delta F \cong \{ [f(\rho_l) - f(\rho_v)] / (\rho_l - \rho_v) \} (s/\lambda). \quad (39)$$

In the case of a very large droplet, the interfacial zone will be locally effectively planar. The width parameter \bar{l} then should have attained some finite limiting value independent of s , and should be instru-

²⁰ J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworth's Scientific Publications Ltd., London, 1959), p. 82.

²¹ Expression (29) is intended only as an asymptotic representation valid in the immediate neighborhood of the critical point, and for certain more demanding purposes than envisioned here would require further terms in the development. Equation (29) does not imply (but is implied by) the scaling laws of Refs. 14 and 15.

²² Reference 20, pp. 79-80.

mental in producing a planar surface tension, or free energy γ_∞ . In order to pass on to the next order of precision in which ΔF must exhibit surface contributions to leading order (R may be considered the large parameter near ΔF 's minimum), take now the first term in the last member of (35) to one further order and include the latter two terms to leading order ($\Delta T = T_c - T$):

$$\Delta F(R, \bar{l}) \cong \frac{4\pi R^3}{3} \left[f \left(\rho_v + \frac{3s}{4\pi\lambda R^3} \right) - f(\rho_v) \right] - 4\pi R^2 \bar{l} [f(\rho_l) - f(\rho_v)] + \frac{9Bs^2}{16\pi\lambda^2 \bar{l} R^4} + \left(\frac{32\pi^2 \lambda \bar{l} R^5}{3s} \right) I(\Delta T); \quad (40)$$

$$I(\Delta T) = \int_{\rho_v}^{\rho_l} \{ f(\rho) - f(\rho_v) \} d\rho. \quad (41)$$

Here the integral has been simplified somewhat by conversion to density as an integration variable, and in the surface terms containing \bar{l} we have permitted the replacement of ρ_i by ρ_l without error in the requisite order. From Eq. (29) one calculates

$$I(\Delta T) = \frac{f_1 f_2}{f_4} (\Delta T)^{2\beta} + \frac{2^{3/2} f_2^{5/2}}{15 f_4^{3/2}} (\Delta T)^{\gamma+3\beta}. \quad (42)$$

The minimization of ΔF in Eq. (40) with respect to \bar{l} is especially simple:

$$0 = (\partial \Delta F / \partial \bar{l})_R = -4\pi R^2 [f(\rho_l) - f(\rho_v)] - \frac{9Bs^2}{16\pi\lambda^2 R^4 \bar{l}^2} + \frac{32\pi^2 \lambda R^5 I(\Delta T)}{3s}. \quad (43)$$

In solving this last equation for \bar{l}^2 , it suffices to use the previous-order estimate (38) to eliminate R . Thus we obtain

$$\bar{l}^2 = \frac{B(\rho_l - \rho_v)^3}{8I(\Delta T) - 4(\rho_l - \rho_v)[f(\rho_l) - f(\rho_v)]} = 15B/8f_2(\Delta T)^\gamma. \quad (44)$$

When \bar{l} is fixed at this value, the free energy (40) may be put into the following suggestive form:

$$F(R) = \frac{4\pi R^3}{3} \left[f \left(\rho_v + \frac{3s}{4\pi\lambda R^3} \right) - f(\rho_v) \right] + 4\pi\gamma_\infty R^2, \quad (45)$$

$$\gamma_\infty = (8Bf_2^3/15f_4^2)^{1/2} (\Delta T)^{\frac{1}{2}\gamma+2\beta}. \quad (46)$$

Indeed γ_∞ may properly be identified as the (planar) surface tension since the remaining variational problem is the one encountered before except for inclusion now of an extra surface (i.e., R^2) term tending to reduce the equilibrium radius. One easily finds the corrected radius to be

$$R(s) = R_\infty (s/\lambda)^{1/3} - \delta R, \quad \delta R = [2\gamma_\infty/3(\rho_l - \rho_v)^2 f''(\rho_l)] = (B/270f_2)^{1/2} (\Delta T)^{-\gamma/2}, \quad (47)$$

up to terms which vanish as $s \rightarrow \infty$.

Now that the interfacial zone has explicitly been taken into account (at least in the locally planar approximation), it is clear that the free energy must now be correct both for cluster bulk contributions proportional to s/λ [already given correctly in Eq. (39)], and for surface contributions varying as $(s/\lambda)^{2/3}$. Actually, the variational stationariness property of ΔF implies that the \bar{l} and R results (44) and (47) will even correctly give ΔF through $(s/\lambda)^{1/3}$ order. At the ΔF minimum, the free energy may be expressed as a quadratic form in R and \bar{l} variations:

$$\Delta(\Delta F) \cong A_1(s) (\Delta R)^2 + A_2(s) (\Delta R) (\Delta \bar{l}) + A_3(s) (\Delta \bar{l})^2. \quad (48)$$

Since extension of our iterative procedure would result in development of both $R(s)$ and $\bar{l}(s)$ in series of descending powers of $(s/\lambda)^{1/3}$, and since $(s/\lambda)^{-1/3}$ is the first order so far neglected for both, we may interpret ΔR and $\Delta \bar{l}$ as the errors in R and \bar{l} of this order committed in Eqs. (44) and (47). Since \bar{l} variations at constant R change interfacial structure, $A_3(s)$ must be proportional to $s^{2/3}$ for large s . Similarly, the thermodynamic assessment of pure R variation assures that the large- s behavior of $A_1(s)$ is proportional to $s^{1/3}$. Because Expression (48) must be positive definite, $A_2(s)$ can diverge at large s no faster than $s^{2/3}$. Therefore with the cited ΔR and $\Delta \bar{l}$, Eq. (48) predicts that at large s , the error in ΔF obtained by simply substituting our earlier R and \bar{l} results into Eq. (35) will be bounded, i.e., will not affect $s^{1/3}$ terms in ΔF .

The manipulative details in the actual substitution are tedious, so we merely exhibit the result:

$$\Delta F = F_1(s/\lambda) + F_2(s/\lambda)^{2/3} + F_3(s/\lambda)^{1/3} + \dots; \quad (49)$$

$$F_1 = [f(\rho_l) - f(\rho_v)] / (\rho_l - \rho_v),$$

$$F_2 = 4\pi\gamma_\infty R_\infty^2,$$

$$F_3 = 4\pi\gamma_{\text{curv}} R_\infty. \quad (50)$$

The F_1 and F_2 coefficients were already obtained, and F_3 has been cast into the form of a surface-tension curvature correction with

$$\gamma_{\text{curv}} = (Bf_2/45f_4) (\Delta T)^{2\beta}. \quad (51)$$

The whole point of this Section's calculation is to establish that the third term in (49) does not dominate the second, for clusters of average size, in the $\Delta T \rightarrow 0$ limit. In the detailed analysis to follow, we actually find that the large- s cluster free energy contains terms of form $\ln s$, which cannot arise in the present context, and these logarithmic contributions are decisive in determining critical phenomena. Although formally $s^{1/3}$ dominates $\ln s$ as $s \rightarrow \infty$, it proves especially useful to disregard the very large number of $s^{1/3}$ terms that arise. The justification for this seemingly inconsistent procedure rests upon the observation that a simple change of variable,

$$s' = s + s_0, \quad (52)$$

with properly chosen s_0 can annihilate the one-third power term, while at the same time leaving two-thirds power and logarithmic terms unchanged so far as coefficients are concerned. Since s or s' occur below merely as summation variables of which only very large values are of importance, we see that disregard of $s^{1/3}$ terms is justified if s_0 remains bounded as $\Delta T \rightarrow 0$, and this criterion is equivalent to

$$\lim_{\Delta T \rightarrow 0} \frac{F_3(s/\lambda)^{1/3}}{F_2(s/\lambda)^{2/3}} \Big|_{s=\bar{s}(\Delta T)} < \infty. \quad (53)$$

$\bar{s}(\Delta T)$ stands here for the mean cluster size at the given temperature.

Later (Sec. VII) we justify identification of the mean cluster diameter with the so-called correlation length varying as $(\Delta T)^{\nu'}$, $\nu' > 0$. Thus

$$R_\infty(\bar{s}/\lambda)^{1/3} \sim (\Delta T)^{\nu'}, \quad \bar{s} \sim (\Delta T)^{\beta-3\nu'}. \quad (54)$$

The left member of Eq. (53) is

$$\lambda^{1/3} \lim_{\Delta T \rightarrow 0} \frac{\gamma_{\text{curv}}}{\gamma_\infty R_\infty(\bar{s})^{1/3}} = (\text{const}) \lim_{\Delta T \rightarrow 0} (\Delta T)^{\nu'-1/3}. \quad (55)$$

We wish therefore to have the exponent $\nu' - \frac{1}{3} > 0$. Although expressions for ν' and γ' are derived below, we may tentatively test the exponent by use of three-dimensional Ising-model results²³:

$$\begin{aligned} \gamma' &\cong \gamma \cong 1.25, \\ \nu' &\cong \nu \cong 0.645. \end{aligned} \quad (56)$$

By a small margin the desired inequality is satisfied.

We therefore proceed under the assumption that indeed $s^{1/3}$ free-energy contributions are negligible.

IV. SURFACE-WAVE COLLECTIVE COORDINATES

We begin now in earnest the detailed microscopic theory of condensation and critical phenomena via physical clusters. At first we exploit simplifications available at low temperatures, so as to establish the trend of development in the most straightforward terms. Subsequently the elaborations required by increasing T to T_c will be incorporated.

Around the thermodynamic triple-point temperature, the vapor phase will be sufficiently dilute that the cavity free energy W_s appearing in the exact cluster partition function should be very small; i.e., the clusters will be essentially isolated and independent. We shall therefore temporarily disregard this function. Also in this low-temperature regime, the physical clusters should manifest only minor deviations from the ideal spherical shape assumed by a liquid droplet under the influence of its surface tension.

For reasonably large numbers of molecules in the cluster, certain motions of the cluster should be accurately described by macroscopic hydrodynamics. Indeed our point of view is simply that oscillations of the droplet about the spherical shape constitute an important class of collective coordinates. Formally let us perform a canonical coordinate transformation from the conventional particle positions $\mathbf{r}_1 \cdots \mathbf{r}_s$ and momenta $\mathbf{p}_1 \cdots \mathbf{p}_s$ to collective coordinates $\xi_1 \cdots \xi_{3s}$ and canonically conjugate momenta $\eta_1 \cdots \eta_{3s}$. Thus

$$\begin{aligned} Z_s &= h^{-3s} (s!)^{-1} \int_{(\text{conn})} \cdots \int \exp \left\{ \frac{-H_s(\xi_1 \cdots \eta_{3s})}{kT} \right\} d\xi_1 \cdots d\eta_{3s} \\ &= \frac{(2\pi s m_0 kT)^{3/2} V}{s! h^{3s}} \int_{(\text{conn})} \cdots \int \exp \left\{ \frac{-H_s(\xi_1 \cdots \eta_{3s})}{kT} \right\} d\xi_1 \cdots d\eta_{3s}. \end{aligned} \quad (57)$$

We have let H_s stand for the s -particle Hamiltonian expressed in the new variables, and have exercised the option of identifying $\xi_1, \xi_2,$ and ξ_3 as the center-of-mass coordinates and $\eta_1, \eta_2,$ and η_3 as the total momentum components.

The computation of the oscillation frequencies of an incompressible liquid droplet with surface tension acting as restoring force is a standard textbook exercise.²⁴ The normal modes correspond to radial deviations of the sphere that are spatially the individual spherical harmonics $Y_{l,m}(\theta, \phi)$, and whose frequencies depend on l , but not m :

$$\omega(l, m) = [l(l-1)(l+2)(4\pi\gamma_1/3m_0s)]^{1/2}. \quad (58)$$

γ_1 is the undisturbed droplet's mechanical surface tension, which we do not attempt to evaluate in this work, but which will ultimately be superseded by the

measurable surface tension of the planar liquid-vapor interface.

The next step consists in identifying a subset of the remaining collective variables with these droplet oscillations. It is clearly desirable to limit l ,

$$2 \leq l \leq l_{\text{max}}, \quad (59)$$

so as to prevent the surface distortions from having wavelengths less than the distance between neighboring molecules in the droplet, for otherwise the hydrodynamic calculations could hardly apply. This requires that l_{max} vary essentially as $s^{1/3}$ for large droplets, so that accounting for degeneracy $2l+1$ of the frequencies (58), the number of surface normal modes will vary asymptotically as $\alpha^2 s^{2/3} = t$, with α^2 a suitable positive constant.

The presumption of independent normal modes of surface oscillation is equivalent to a splitting of Hamiltonian H_s into two distinct parts,

$$H_s(\xi_1 \cdots \eta_{3s}) = H_s^{(0)}(\xi_1 \cdots \eta_3) + H_s^{(2)}(\xi_{4+1} \cdots \eta_{3s}), \quad (60)$$

²³ M. E. Fisher, Natl. Bur. Std. Misc. Publ. 273, 23 (1966). The unprimed indices refer to the same quantities above T_c .

²⁴ H. Lamb, *Hydrodynamics* (Cambridge University Press, Cambridge, England, 1930), p. 450.

the former of which has independent harmonic-oscillator form for the surface modes:

$$H_s^{(1)}(\xi_1 \cdots \eta_l) = \sum_{i=1}^l \frac{1}{2} \left(\omega_i^2 \xi_i^2 + \frac{\eta_i^2}{m_i} \right) \quad (61)$$

(m_i is the "mass" of the i th mode) and the latter of

which contains *only* the remaining collective coordinates. $H_s^{(2)}$ may therefore be identified as the droplet bulk-phase Hamiltonian.

The surface mode coordinates may now be integrated in expression (57) to yield a product of classical harmonic-oscillator partition functions:

$$Z_s = \frac{(2\pi s m_0 kT)^{3/2} V}{s! h^{3s-l+3}} \left[\prod_{i=1}^l \frac{kT}{\hbar \omega_i} \right] \int_{(\text{conn})} \cdots \int \exp \left\{ \frac{-H_s^{(2)}(\xi_{l+1} \cdots \eta_{3s})}{kT} \right\} d\xi_{l+1} \cdots d\eta_{3s}. \quad (62)$$

For large s , the dominant fraction of the collective coordinates are bulk, not surface, modes. The free energy of these bulk modes (with all surface modes constrained to zero amplitude) should have a large- s development of the following type:

$$(s! h^{3s-l})^{-1} \int_{(\text{conn})} \cdots \int \exp \left\{ \frac{-H_s^{(2)}(\xi_{l+1} \cdots \eta_{3s})}{kT} \right\} d\xi_{l+1} \cdots d\eta_{3s} \\ \sim \exp \{ -[a_0(T)s + (6\pi^{1/2} v_0)^{2/3} \gamma_1(T) s^{2/3} + C_1(T) s^{1/3} + kT \alpha_0(T) \ln s + C_2(T)] (kT)^{-1} \}. \quad (63)$$

The terms have been arranged in descending order, with the extensive bulk free energy of the cluster-forming liquid first followed by (a) the surface free energy of the undeformed spherical surface, whose area is $(6\pi^{1/2} v_0)^{2/3} s^{2/3}$ when expressed in terms of the volume per molecule v_0 of the droplet liquid; (b) the surface-tension curvature correction; (c) possible logarithmic terms as arise for example even from asymptotic expansion of $s!$ by Stirling's formula; (d) an s -independent constant term.

The entire cluster free energy, including center-of-mass motion and surface modes, follows from insertion of frequencies (58), and bulk free energy (63), into Z_s in Eq. (62),

$$-kT \ln Z_s = a_0 s + (6\pi^{1/2} v_0)^{2/3} \gamma_1 s^{2/3} + C_1 s^{1/3} + kT \alpha_0 \ln s + C_2 \\ -kT \ln \left[\frac{(2\pi s m_0 kT)^{3/2} V}{h^3} \right] + \frac{1}{2} (kT) \sum_{l=2}^{l_{\max}} (2l+1) \ln \left[\frac{4\pi \gamma_1 l(l-1)(l+2)}{3m_0 s} \left(\frac{\hbar}{kT} \right)^2 \right]. \quad (64)$$

We see that the center-of-mass term contributes both to the $\ln s$ and the constant (i.e., s^0) parts of the free energy. The l sum in Eq. (64), arising from the surface modes, will contribute to order $s^{2/3}$ and lower orders in s , since these modes are $s^{2/3}$ in number substantially.

Although this last expression seems complicated, while at the same time to contain several unevaluated quantities, we emphasize that important simplifications are available for the present inquiry. It has already been remarked that the totality of $s^{1/3}$ terms should be negligible in passing to the critical point. Furthermore, along the coexistence curve the bulk free energy $a_0 s$ in Eq. (64) will be precisely canceled in the fundamental density expression (2) by $s\mu$, this being in fact the low-temperature criterion for condensation. Finally the magnitude of constant terms such as C_2 will have no bearing upon the critical region exponent relations to be derived below.

In the light of these considerations, then, the surface-mode sum in Eq. (64) becomes elevated to a position of special prominence in probing condensation and critical phenomena. Considerable care therefore must be exercised in developing that sum in an asymptotic large- s series so as to capture the correct $s^{2/3}$ and $\ln s$ contributions to cluster free energy that it generates. Of course our considerations thus far have been restricted to the low-temperature region, and in fact two modifications of Eq. (64) are required at elevated

temperature. We reserve the asymptotic development of the surface-mode sum in Eq. (64) until the next section, so as simultaneously to incorporate the modifications.

Since surface tension decreases as temperature increases, while at the same time the mean energy of the surface modes increases, it is certain that these modes will no longer act as independent oscillators. The next section contains details of a proposal for treating this mode interaction in a self-consistent fashion. The other requisite high-temperature modification is inclusion of the now nonnegligible cavity free energy W_s in the cluster partition function which we now attempt to assess. Reference 11 contains an exact cluster expansion (of the Mayer type) for W_s .²⁵ In order to account for the leading order effects, and therefore to establish the qualitative trend as T approaches T_c , we can treat the assembly of clusters surrounding the s -cluster of interest as a dilute set of spheres, each of which is excluded from the neighborhood of the s -cluster by the non-overlap restriction. Details of the calculation, which entails the differential geometry of a perfect-sphere rolling on another sphere with surface-mode distortion are far too tedious and uninformative to include here. The result for W_s may be developed in descending powers of $s^{1/3}$ (without a logarithmic term); for our

²⁵ Reference 11, Eqs. (27) and (29).

purposes, only the contributions proportional to s and $s^{2/3}$ need be retained:

$$W_s \cong \left[kT \sum_{s'=1}^{\infty} \frac{N_{s'}}{V} \right] (v_0 s) + \left[kT \left(\frac{3v_0}{4\pi} \right)^{1/3} \sum_{s'=1}^{\infty} \frac{(s')^{1/3} N_{s'}}{V} \right] (S_s + \Delta S_s). \quad (65)$$

S_s is the surface area of the droplet in its undistorted state, $(6\pi^{1/2}v_0s)^{2/3}$, and ΔS_s its increase due to the surface-mode distortions. The two terms shown for W_s thus have an obvious interpretation: the first is the pressure-volume work (in the free-cluster ideal-gas approximation) that would macroscopically be required to empty the s -cluster's cavity, and the second is a positive surface-tension contribution arising from cluster interference at the cavity surface. If a more accurate calculation of W_s were made, an improvement of the ideal-gas pressure would surely result, as well as a more complicated surface-tension contribution.

If W_s in form (65) is inserted into Z_s , the result is first to shift the bulk free energy a_0s in Eq. (64) to $(a_0 + pv_0)s$, and so condensation would now be predicted to occur when μs equals this shifted bulk free energy. Furthermore, the cluster-surface-area increment is a diagonal quadratic form in surface-mode amplitudes, so not only does the second term in (65) "renormalize" γ_1 in the second term of Eq. (64) but it also modifies in the same way the γ_1 that establishes surface mode frequencies which occur in the last term of Eq. (64). Both γ_1 occurrences may therefore be replaced by a new surface tension γ_2 , which now may be considered to properly account for cluster interference effects on the surface-mode spectrum; the approximate cluster exclusion calculation estimates

$$\gamma_2 \cong \gamma_1 + \left(\frac{3v_0}{4\pi} \right)^{1/2} \sum_{s'=1}^{\infty} \frac{(s')^{1/3} N_{s'}}{V}. \quad (66)$$

V. SURFACE-TENSION INTEGRAL EQUATION

The contribution of order $s^{2/3}$ to the cluster free energy (64) provided by collective surface modes should be small at low temperature (the l sum is multiplied by T). However as T is raised, the effect of these modes likewise increases to produce a substantial shift of the surface tension γ_2 . To suppose on the one hand that surface modes remain decoupled, while at the same time using them to predict a large surface-tension effect on γ_2 is in fact inconsistent. Surely the proper surface tension to utilize in the frequency formula (58) for long-wavelength oscillations of a large droplet would be the measurable surface tension, which includes the effect of the oscillations themselves. We now construct a self-consistent scheme for such high-temperature effects which implicitly accounts for normal-mode interaction near T_c , but reduces automatically at low T to an independent surface-mode description.

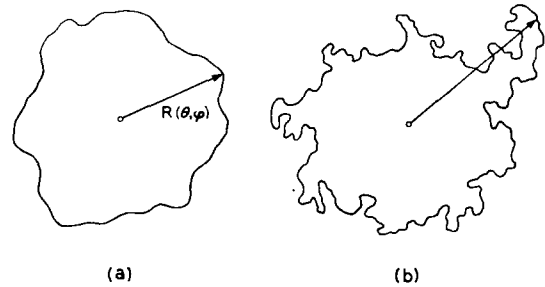


FIG. 6. (a) Slightly distorted spherical droplet surface at low temperature with single-valued radius function $R(\theta, \phi)$. (b) Highly contorted, multiple-valued surface structure near T_c .

The central concept we use concerns sequential placing of surface mode distortions on an initially spherical droplet, starting at the large- l end of the spectrum, and working downward to the smallest l 's. The appropriate frequency-determining surface tension at the beginning of this process is γ_2 , but as it proceeds γ_2 is modified by virtue of modes already placed to $\gamma_2 q_2(l/l_{\max})$ [where of course $q_s(1) = 1$], and where the function $q_s(x)$ must be self-consistently determined. The macroscopic surface tension γ_∞ may then be identified as

$$\gamma_\infty = \lim_{s \rightarrow \infty} \gamma_2 q_s(2/l_{\max}), \quad (67)$$

and so involves the effects of the full surface-mode spectrum. If we now set, for s -cluster surface-mode frequencies,

$$\tilde{\omega}_s(l) = \left[l(l-1)(l+2) \frac{4\pi\gamma_2 q_s(l/l_{\max})}{3m_0s} \right]^{1/2} \quad (68)$$

as is required by the previous hydrodynamic result (58), then the self-consistent requirement which determines q_s is the following ($2 \leq l < l_{\max}$):

$$\exp \left[\frac{-\gamma_2 q_s(l/l_{\max}) (6\pi^{1/2}v_0s)^{2/3}}{kT} \right] = \left\{ \prod_{l'=l+1}^{l_{\max}} \left[\frac{kT}{\hbar\tilde{\omega}_s(l')} \right]^{2l'+1} \right\} \exp \left\{ \frac{-\gamma_2 (6\pi^{1/2}v_0s)^{2/3}}{kT} \right\}. \quad (69)$$

One of the requirements posed by the presumption of independent surface modes is that droplet radius must be a single-valued function of angles so as to permit a unique spherical harmonic resolution. This will surely be valid at sufficiently low temperature, but as T_c is approached, it is reasonable instead to expect that the droplet surface should become extremely convoluted with irregular fissures and filaments as shown in Fig. 6. The sequential mode addition procedure permits these complicated surface structures to form as the result of local addition of many surface perturbations, no one of which need be very large. The idea therefore is that imposition of a long-wavelength (i.e., small l) disturbance locally stretches and tips the cluster surface with whatever fine-grained convolutions it had to that point already accumulated.

A nonlinear equation for q_s results from taking

logarithms in Eq. (69), after insertion of $\bar{\omega}_s(l)$ from Eq. (68):

$$q_s\left(\frac{l}{l_{\max}}\right) = 1 + \frac{kT}{(6\pi^{1/2}v_0s)^{2/3}\gamma_2} [(l_{\max}+1)^2 - (l+1)^2] \ln \left[\frac{\hbar}{kT} \left(\frac{4\pi\gamma_2}{3m_0} \right)^{1/2} \right] \\ + \frac{kT}{2(6\pi^{1/2}v_0s)^{2/3}\gamma_2} \sum_{l'=l+1}^{l_{\max}} (2l'+1) \ln \left[\frac{l'(l'-1)(l'+2)}{s} \right] + \frac{kT}{2(6\pi^{1/2}v_0s)^{2/3}\gamma_2} \sum_{l'=l+1}^{l_{\max}} (2l'+1) \ln q_s\left(\frac{l'}{l_{\max}}\right). \quad (70)$$

In order to observe the implications of our sequential mode addition procedure for surface tension in the planar macroscopic limit, set

$$x = l/l_{\max}, \\ l_{\max} = \alpha s^{1/3}, \\ q(x) = \lim_{s \rightarrow \infty} q_s(x). \quad (71)$$

Then upon permitting s to go to infinity in Eq. (70), the l' sums pass into integrals to yield finally a non-linear integral equation for $q(x)$:

$$q(x) = 1 + AT \\ \times \left[\ln(DT)(x^2 - 1) - \frac{3}{2}x^2 \ln x + \int_x^1 y \ln q(y) dy \right], \quad (72)$$

where

$$A = [\alpha^2 k / (6\pi^{1/2}v_0)^{2/3}\gamma_2], \\ D = (ke^{3/4}/\hbar\alpha^{3/2})(3m_0/4\pi\gamma_2)^{1/2}. \quad (73)$$

Although the quantities A and D will be somewhat temperature dependent, it should be permissible to regard them essentially as constants for inquiry into the nature of the solution to (72). In the low-temperature limit, then, the bracketed term in this integral equation is greatly diminished by the factor AT preceding it, so an iteration should be valid. In the low- T regime, we thus conclude

$$q(x, T) \sim 1 + AT \{ \ln(DT)(x^2 - 1) - \frac{3}{2}x^2 \ln x \} \\ + O(T^2 \ln T). \quad (74)$$

Therefore the x variation of q , resulting from mode coupling in the sequential addition scheme, declines in magnitude as T approaches zero to leave $q(x, 0) \equiv 1$, corresponding precisely to independent surface modes.

The low-temperature form shown in Eq. (74) indicates that although the initial effect of mode coupling is to raise $q(0, T)$ above unity, eventually it begins to decline (when T exceeds D^{-1}), and since we know that surface tension vanishes at the critical point, T_c must be identified as that temperature at which $q(0, T) = 0$. The expected behavior is shown qualitatively in Fig. 7.

For all $T < T_c$, we have the small- x asymptotic behavior:

$$q(x, T) \sim q(0, T) - Q_1(T)x^2 \ln x + Q_2(T)x^2;$$

If this is substituted into the integral equation (72),

one finds

$$q(0, T) = 1 + AT \left[-\ln(DT) + \int_0^1 y \ln q(y, T) dy \right], \\ Q_1(T) = \frac{3}{2}AT, \\ Q_2(T) = AT \ln \{ DT / [q(0, T)]^{1/2} \}. \quad (75)$$

However, at T_c one easily obtains

$$q(x, T_c) \sim -\frac{5}{2}AT_c x^2 \ln x - \frac{1}{2}AT_c x^2 \ln \ln(1/x) + O(x^2). \quad (76)$$

The discontinuous jump in $Q_1(T)$ at T_c , as well as the change in functional form, is heralded by the divergence in $Q_2(T)$ as T approaches T_c .

The aptness of different surface tensions for different disturbance wavelengths is intimately related to the surface fluctuation theorem derived and discussed in Appendix A. Because this theorem represents an interfacial analog of the familiar fluctuation-compressibility relationship for homogeneous fluids,²⁶ it is hardly surprising that $q(x, T)$ should be singular at T_c , since the homogeneous-phase susceptibilities are singular.

The sequential mode addition approach may be considered an alternative to the temperature-dependent cutoff suggestion proposed earlier in Refs. 10 and 12 for rough assessment of critical-region-mode interaction.

VI. ASYMPTOTIC FORM OF Z_s

Although the $l=2$ modes are those of smallest l for physical clusters, it is convenient to extend Eq. (69) to the case $l=1$. Indeed we see from Eqs. (62) and (63) that the surface-mode contribution to Z_s is equivalent to

$$\exp \left[\frac{-\gamma_2 q_s(1/l_{\max})(6\pi^{1/2}v_0s)^{2/3}}{kT} \right] \\ = \left\{ \prod_{l'=2}^{l_{\max}} \left[\frac{kT}{\hbar\bar{\omega}_s(l')} \right]^{2l'+1} \right\} \exp \left\{ \frac{-\gamma_2(6\pi^{1/2}v_0s)^{2/3}}{kT} \right\}. \quad (77)$$

It will be required to evaluate this quantity to the correct power of s in the large- s asymptotic regime, or equivalently the correct coefficient of $s^{-2/3} \ln s$ in asymptotic evaluation of $q_s(1/l_{\max})$.

In order to effect the necessary accurate calculation,

²⁶ L. S. Ornstein and F. Zernike, Koninkl. Ned. Akad. Wetensch. Proc. Ser. B 17, 793 (1914); J. Yvon, *Fluctuations en Densité, Actualités Scientifique et Industrielles*, No. 542 (Hermann & Cie., Paris, 1937). The generalization to finite wavelength fluctuations and external perturbations was pointed out by P. G. deGennes, *Nuovo Cimento* 9, Suppl. 1, 240 (1958).

first rewrite Eq. (70) as follows:

$$q_s(x) = 1 + AT \left[\left(1 + \frac{1}{\alpha s^{1/3}} \right)^2 - \left(x + \frac{1}{\alpha s^{1/3}} \right)^2 \right] \ln \left[\frac{\hbar}{kT} \left(\frac{4\pi\gamma_2}{3m} \right)^{1/2} \right] + \frac{AT}{\alpha^2 s^{2/3}} \left\{ \Delta(s, l) + \frac{1}{2} \int_{l+1/2}^{\alpha s^{1/2} + 1/2} d\ell' (2\ell' + 1) \ln \left[\frac{\ell'(\ell' - 1)(\ell' + 2)}{s} \right] \right\} + \frac{AT}{2\alpha^2 s^{2/3}} \sum_{\ell' = l+1}^{l_{\max}} (2\ell' + 1) \ln q_s(\ell'/l_{\max}). \tag{78}$$

The quantity $\Delta(s, l)$ stands for the error incurred in replacement of the first l sum in Eq. (70) by an integral:

$$\Delta(s, l) = \frac{1}{2} \sum_{\ell' = l+1}^{l_{\max}} (2\ell' + 1) \ln \left[\frac{\ell'(\ell' - 1)(\ell' + 2)}{s} \right] - \frac{1}{2} \int_{l+1/2}^{l_{\max} + 1/2} d\ell' (2\ell' + 1) \ln \left[\frac{\ell'(\ell' - 1)(\ell' + 2)}{s} \right]. \tag{79}$$

It is a relatively easy matter to obtain the large- s behavior of Δ by breaking the integral into a sum of integrals over unit intervals, and Taylor-expanding the integrands about the midpoints, through quadratic order:

$$\Delta(s, l) \sim \Delta_0(l) - \frac{1}{8} \ln(\alpha s^{1/3}/l). \tag{80}$$

Here, the function $\Delta_0(l)$ is independent of s and of little importance in the following. We see therefore that even replacement of sums by integrals can produce contributions of the important “lns” type.

Next calculate the integral remaining in Eq. (78):

$$I(s, l) = \frac{1}{2} \int_{l+1/2}^{\alpha s^{1/2} + 1/2} d\ell' (2\ell' + 1) \ln \left[\frac{\ell'(\ell' - 1)(\ell' + 2)}{s} \right] = s^{2/3} \left\{ \int_{(l+1/2)s^{-1/3}}^{\alpha + (1/2)s^{1/3}} y \ln y dy + \int_{(l-1/2)s^{-1/3}}^{\alpha - (1/2)s^{1/3}} y \ln y dy + \int_{(l+1/2)s^{-1/3}}^{\alpha + (5/2)s^{1/3}} y \ln y dy \right\} + s^{1/3} \left\{ \frac{1}{2} \int_{(l+1/2)s^{-1/3}}^{\alpha + (1/2)s^{1/3}} \ln y dy + \frac{3}{2} \int_{(l-1/2)s^{-1/3}}^{\alpha - (1/2)s^{1/3}} \ln y dy - \frac{3}{2} \int_{(l+1/2)s^{-1/3}}^{\alpha + (5/2)s^{1/3}} \ln y dy \right\}. \tag{81}$$

When l is of order 1, we find by performing the integrals here that the large- s form of $I(s, l)$ is

$$I(s, l) \sim \frac{3}{2} \alpha^2 (\ln \alpha - \frac{1}{2}) s^{2/3} + (3\alpha \ln \alpha - \frac{1}{2} \alpha) s^{1/3} + (\frac{1}{2} l^2 + l - \frac{7}{24}) \ln s + I_0(l), \tag{82}$$

where $I_0(l)$ is an s -independent function of l . We note in passing that a different asymptotic development is necessary for large s if $x = l/\alpha s^{1/3}$, rather than l , is held fixed:

$$I \sim \left\{ \frac{3}{2} \alpha^2 [\ln \alpha - \frac{1}{2}] - \frac{3}{2} \alpha^2 x^2 [\ln(\alpha x) - \frac{1}{2}] \right\} s^{2/3} + \left\{ 3\alpha \ln \alpha - \frac{1}{2} \alpha - 3\alpha x \ln(\alpha x) + \frac{1}{2} (\alpha x) \right\} s^{1/3} + I_1(\alpha, x), \tag{82'}$$

where now I_1 is s independent. The nonoccurrence of a lns term may be attributed to the fact that the fixed- x limit operation avoids the previous fixed- l feature that the lower integration limit converges to a logarithmic infinity of the integrand.²⁷

In order to evaluate the quantity (77), we must examine Eq. (78) for x of order $s^{-1/3}$. For this purpose we use results (80) and (82) to obtain

$$q_s(x) = 1 + AT \left\{ (1 - x^2) \ln \left[\frac{\hbar}{kT} \left(\frac{4\pi\gamma_2}{3m_0} \right)^{1/2} \right] + \frac{3}{2} \ln(\alpha - \frac{1}{2}) \right\} + \frac{AT}{\alpha s^{1/3}} \left\{ (2 - 2x) \ln \left[\frac{\hbar}{kT} \left(\frac{4\pi\gamma_2}{3m_0} \right)^{1/2} \right] + 3 \ln \alpha - \frac{1}{2} \right\} + \frac{AT}{\alpha^2 s^{2/3}} \left[\frac{1}{2} l^2 + l - \frac{1}{3} \right] \ln s + \frac{AT}{\alpha^2 s^{2/3}} \sum_{\ell' = l+1}^{l_{\max}} (\ell' + \frac{1}{2}) \ln q_s(\ell'/l_{\max}). \tag{83}$$

Here we have dropped some $s^{-2/3}$ terms in the interest of relative compactness, since they would provide only constant multipliers for Z_s which are of no direct interest in the present context.

Below T_c , $\ln q(x)$ is smooth and bounded over $0 \leq x \leq 1$, so for sufficiently large s the same should be

true of $\ln q_s(x)$. Therefore below T_c , the ℓ' sum in (83) should be sufficiently regular to give rise to *no* lns terms. Then Eq. (83) predicts

$$q_s \left(\frac{1}{l_{\max}} \right) \sim q(0) + (\text{const}) s^{-1/3} + \frac{7AT}{6\alpha^2 s^{2/3}} \ln s + \frac{\text{const}}{\alpha^2 s^{2/3}}. \tag{84}$$

We have already argued that terms of the same type as the second in the right-hand member here could be disregarded. Consequently, Eq. (84) in connection with

²⁷ The lns term found in Eq. (80) for fixed l is likewise associated with the logarithmic divergences of the summand and integrand of $\Delta(s, l)$ near the origin.

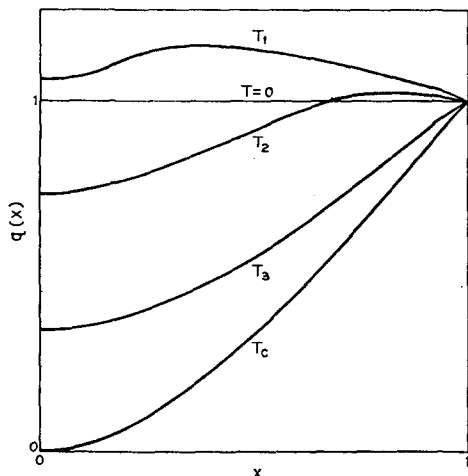


FIG. 7. Qualitative trend of surface-tension dispersion function $q(x, T)$, resulting from the sequential-mode addition procedure, for an ascending set of temperatures, $0 < T_1 < T_2 < T_3 < T_c$. For all temperatures $q(1, T) = 1$.

Eqs. (77), (63), and (62) imply for large s that

$$\exp\left(\frac{s\mu}{kT}\right) Z_s(T, \mu) \sim (\text{const}) V s^{1/3 - \alpha_0} \times \exp[-\gamma_\infty(T) (6\pi^{1/2} v_{0s})^{2/3}] \quad (85)$$

along the coexistence curve.

Next, we examine the situation at T_c . Now the possibility arises for additional $\ln s$ terms to be generated by the l' sum in (83), since $\ln q(l'/l_{\max})$ at the critical temperature has a logarithmic infinity at $l' = 0$ according to Eq. (76). It should suffice, for estimation of this extra $\ln s$ contribution in the asymptotic large- s limit, to replace $q_s(l'/l_{\max})$ by $q(l'/l_{\max})$.²⁸ Since $q(x, T_c)$ varies as x^2 nears $x = 0$, to the nearest power of x , the $\ln s$ terms may equally well be estimated by using simply x^2 in place of $q(x, T_c)$. Therefore examine the following sum:

$$\frac{AT}{\alpha^2 s^{2/3}} \sum_{l'=2}^{l_{\max}} (2l'+1) \ln\left(\frac{l'}{l_{\max}}\right) = \frac{AT}{\alpha^2 s^{2/3}} \times \left[\Delta_q(s, 1) + \int_{3/2}^{l_{\max}+1/2} (2l'+1) \ln\left(\frac{l'}{l_{\max}}\right) dl' \right]. \quad (86)$$

The defect Δ_q arises in passing from summation to integration, and can be evaluated in the same way as

²⁸ It should be remembered here that the argument in Sec. III essentially shows that difference between $q(x)$ and $q_s(s)$ for x of order $s^{-1/3}$ is itself of order $s^{-1/3}$, being essentially surface-tension curvature correction, and can be annihilated by innocuous variable change. It may furthermore be shown that the next-order difference between $q(x)$ and $q_s(x)$ varying as $s^{-2/3} \ln s$, is too small to affect estimation of the new $\ln s$ droplet free-energy contribution at T_c . It may be worth noting here that an alternative to the curvature-correction annihilating variable shift would be inclusion of an order $s^{1/3}$ correction in cutoff parameter α , whose coefficient could be selected in principle to produce the same effect.

was Δ in Eq. (80):

$$\Delta_q(s, 1) = \sum_{l'=2}^{l_{\max}} (2l'+1) \ln\left(\frac{l'}{l_{\max}}\right) - \int_{3/2}^{l_{\max}+1/2} (2l'+1) \ln\left(\frac{l'}{l_{\max}}\right) dl' \sim \text{const} - (1/36) \ln s. \quad (87)$$

The l' integral in Eq. (86) is elementary, and gives a result of the form

$$(\text{const}) s^{2/3} + (\text{const}) s^{1/3} + \frac{5}{4} \ln s + \text{const}. \quad (88)$$

We can combine the $\ln s$ coefficients in these last two equations to obtain a new factor $s^{-11/9}$ in the Z_s asymptote which discontinuously arises at T_c . Thus in place of Eq. (85) we find

$$\exp(s\mu_c/kT_c) Z_s(T_c, \mu_c) \sim (\text{const}) V s^{-(8/9) - \alpha_0}. \quad (89)$$

The exponential factor in (85) of course disappears due to vanishing of the experimental surface tension $\gamma_\infty(T)$ at T_c .

For fixed cluster size s there is of course no discontinuity in $\exp(s\mu/kT) Z_s$ at T_c . In order to reconcile this fact with the exponent shift from (85) to (89), we observe that very close to T_c , the logarithmic summand factor in the key equation (83) roughly behaves for large s near $l' = 0$ as follows:

$$\ln q_s(l'/l_{\max}) \sim \ln[k_1 \gamma_\infty(T) + (l'/l_{\max})^2], \quad (90)$$

where k_1 is a positive constant. This expression interpolates the facts that (a) at $l' \cong 0$, the $q_s \cong q$ must be proportional to the actual surface tension $\gamma_\infty(T)$, and (b) when T is sufficiently close to T_c there can be a substantial l' interval over which q is varying (to the nearest power) just quadratically with l'/l_{\max} , and yet far exceeds in magnitude the value of $q(0)$. If $\gamma_\infty(T)$ is sufficiently small, then for a given s , the summand in Eq. (83) may behave as though only the second term in brackets were present for all $l' \geq 2$, so for this s , Eq. (89) would apply. But at the same temperature [i.e., at the same small $\gamma_\infty(T)$], the two bracketed terms in Eq. (90) are comparable at the lower summation limit ($l' = 2$) when

$$k_1 \gamma_\infty(T) \approx (2/l_{\max})^2 = 4/\alpha^2 s^{2/3},$$

or in other words when

$$s = s^* \approx (\text{const}) [\gamma_\infty(T)]^{-3/2}. \quad (91)$$

For even larger s , the subdivisions implicit in the l'/l_{\max} sum are so close to one another that the full form (90) is required, and since this latter is smooth and bounded near $l'/l_{\max} = 0$, Eq. (85) applies. The smooth transition around s values shown in (91) may in sufficient accuracy be exhibited by the following

interpolation formula valid along the coexistence curve:

$$\begin{aligned} \exp(s\mu/kT) Z_s(T, \mu) &\sim (\text{const}) V s^{1/3-\alpha_0} [\gamma_\infty(T) + k_2 s^{-2/3}]^{11/6} \\ &\times \exp[-\gamma_\infty(T) (6\pi^{1/2} v_0 s)^{2/3}], \end{aligned} \quad (92)$$

where k_2 is another positive constant. The equations (85) and (89) respectively correspond to allowing $s \rightarrow \infty$ at fixed $T < T_c$, and to allowing $T \rightarrow T_c$ at fixed s .

Formula (92) is central to derivation of the several critical region exponent relations in the next section. However it still contains the unknown index α_0 . Because α_0 arose from the cluster bulk, and because the principal change in cluster morphology in approaching T_c results from sudden increase in just surface mode amplitudes, we can reasonably suppose α_0 is substantially a constant in the critical region. This constant value may then be evaluated easily from the phenomenological surface tension and coexistence-curve laws. From Eqs. (1) and (2) along the coexistence curve, we obtain an expression for the saturated vapor density:

$$\rho_v = \sum_{s=1}^{\infty} s \exp(s\mu_{\text{sat}}/kT) \frac{Z_s(T, \mu_{\text{sat}})}{V}, \quad (93)$$

where μ has been set equal to its value μ_{sat} on the coexistence curve. One can see from the asymptotic estimate (92) that the small- s terms in this last sum will be essentially unchanged if T is only slightly less than T_c , but the exponential term effectively provides an upper cutoff on the sum at the value shown in Eq. (91). Thus

$$\begin{aligned} \rho_v(T) &\cong \rho_c - \sum_{s=s^*}^{\infty} s \exp(s\mu_{\text{sat}}/kT) \frac{Z_s(T, \mu_{\text{sat}})}{V} \\ &\cong \rho_c - (\text{const}) \int_{s^*}^{\infty} s^{(1/3)-\alpha_0} ds \\ &= \rho_c - (\text{const}) (s^*)^{(10/9)-\alpha_0} \\ &= \rho_c - (\text{const}) [\gamma_\infty(T)]^{(3\alpha_0/2)-(5/3)}. \end{aligned} \quad (94)$$

Equation (46) in Sec. III exhibits an estimate of the power law for surface tension vanishing at the critical point. Without for the moment entering into consideration of the merits of that specific estimate, we now simply write

$$\gamma_\infty(T) \sim (\text{const}) (\Delta T)^\sigma, \quad (95)$$

where σ is the phenomenological critical-region exponent, known²⁹ to be close to 1.29. If this surface-tension form is inserted into expression (94), and the result required to yield the coexistence curve exponent β , then α_0 can be equal only to a single possible value:

$$\alpha_0 = 2\beta/3\sigma + 10/9. \quad (96)$$

²⁹ R. A. Lovett and F. P. Buff, in *Simple Dense Fluids; Data and Theory*, Z. W. Salsburg and H. L. Frisch, Eds. (Academic Press Inc., New York, to be published).

We use this phenomenological determined value in the following section.

VII. CRITICAL EXPONENTS

One of the key quantities which arises in the study of critical phenomena is the range of molecular correlation function. If $g^{(2)}(r; T, \mu)$ stands for the molecular correlation function (which has value unity at infinite distance r), then Fisher³⁰ has proposed a convenient form for representation of the large- r approach of $g^{(2)}$ to its limit in the one-phase portion of the critical region:

$$g^{(2)}(r; T, \mu) - 1 \sim (\text{const}) \frac{\exp(-\kappa r)}{r^{1+\eta}} [1 + Q(\kappa r)]. \quad (97)$$

Here, $Q(x) \sim x^\eta$ as x becomes large. The phenomenon of critical opalescence is a direct result of the fact that the exponential decay parameter κ goes to zero at the critical point, and the inverse of κ is obviously a measure of the spatial extent of local density fluctuations in the system. The sequence of moments of $g^{(2)}(r) - 1$ clearly reflect this identification near the critical point:

$$\frac{\int r^n [g^{(2)}(r) - 1] dr}{\int [g^{(2)}(r) - 1] dr} \sim (\text{const}) \kappa^{-n}. \quad (98)$$

The general approach to understanding of critical phenomena through physical clusters suggests a means of determining κ . Below T_c the system consists of an assembly of nearly spherical droplets, whose interior liquid is substantially higher in density than the ambient fluid. In adequate approximation we may suppose that these spherical clusters have positions that are independent of one another to the extent that outside of any given cluster the local molecular density rapidly drops to the macroscopic average. For distances r larger than typical molecular dimensions, $g^{(2)}(r) - 1$ for the random droplet medium will consist of a sum of structure factors S_s for the individual droplets³¹:

$$\begin{aligned} g^{(2)}(r) - 1 &= \sum_{s=1}^{\infty} w(s) S_s(r) \\ &\cong \int_0^{\infty} w(s) S(s^{-1/3}r) ds. \end{aligned} \quad (99)$$

Here we introduce a common cluster-structure function S , appropriately scaled; w is the requisite weight for size- s clusters, which is proportional to the product of cluster volume and cluster density. Along the coexistence curve the latter is just V^{-1} times our previous result (92). Substitution into (99), followed by recalculation of the moments of r^n now yields

$$\frac{\int r^n [g^{(2)}(r) - 1] dr}{\int [g^{(2)}(r) - 1] dr} = (\text{const}) [\gamma_\infty(T)]^{-n/2}. \quad (100)$$

³⁰ M. E. Fisher, *J. Math. Phys.* 5, 944 (1964).

³¹ This result is easily justified by the picturesque Debye procedure of repeatedly throwing a stick of length r into the random medium, and measuring the densities at its ends at each trial; a clear description appears in P. Debye, in *Non-Crystalline Solids*, V. D. Fréchet, Ed. (John Wiley & Sons, New York, 1960), p. 6.

Upon representing the temperature variation of the range parameter κ along the coexistence curve by

$$\kappa = \kappa_0(\Delta T)^{\nu'} \quad (\kappa_0, \nu' > 0), \quad (101)$$

the exponent ν' is required to satisfy

$$\nu' = \frac{1}{2}\sigma \quad (102)$$

to ensure that Eqs. (98) and (100) are consistent.

This last relation has been previously deduced by Widom¹³ from a rather different analysis.

In order to extract further information about critical phenomena from the theory, it is necessary to specify the cluster distribution away from the coexistence curve. In this more general circumstance, γ_∞ fails to be identifiable as an experimentally measurable quantity, and the ambient chemical potential is no longer large enough to cancel exactly the cluster bulk free energy. These extensions now impel us to write the critical-region density expression thus³²:

$$\begin{aligned} \rho(\Delta T, \Delta\mu) = & (\text{const}) \sum_{s=1}^{\infty} s^{(4/3)-\alpha_0} [\gamma_\infty(\Delta T, \Delta\mu) + k_2 s^{-2/3}]^{11/6} \\ & \times \exp\{-[(6\pi^{1/2}v_0)^{2/3} \gamma_\infty(\Delta T, \Delta\mu) s^{2/3} + (a(\Delta T, \Delta\mu) - \mu)s] (kT)^{-1}\}, \end{aligned} \quad (103)$$

where

$$\Delta\mu = \mu_{\text{sat}}(T) - \mu \quad (104)$$

is the chemical potential change measured from the coexistence curve. For $a - \mu$ and γ_∞ in the extended regime, we adopt simple homogeneous functions of ΔT and $\Delta\mu$ as suitable extrapolations:

$$\gamma_\infty(\Delta T, \Delta\mu) = [\gamma_T \Delta T + (\gamma_\mu + \zeta' \gamma_T) \Delta\mu]^\sigma - [\gamma_\mu \Delta T]^\sigma; \quad (105)$$

$$a(\Delta T, \Delta\mu) - \mu = (a_T \Delta T + a_\mu \Delta\mu)^\nu - (a_T \Delta T)^\nu. \quad (106)$$

γ_T , γ_μ , ζ' , a_T , and a_μ are all positive constants, and the new power ν is of course to be positive.

The justification of the γ_∞ expression (105) lies first in its proper reduction to the measurable surface tension when $\Delta\mu = 0$. In addition, it provides for linear variation of γ_∞ with chemical potential at fixed $T < T_c$, reflecting the corresponding linear density change in the medium surrounding a given cluster.³³ Finally the ΔT , $\Delta\mu$ locus defined by setting

$$\gamma_\infty(\Delta T, \Delta\mu) = 0$$

generates the expected boundary in the phase plane across which physical clusters have evaporated out of an asymptotically compact, roughly spherical form to an open spongy network, as remarked at the end of Sec. II.

The bulk free-energy assumption (106) likewise behaves properly at $\Delta\mu = 0$ (for the trivial reason that it vanishes identically), and for fixed positive ΔT it exhibits the linear increase to be expected with increasing $\Delta\mu$. The same linear increase also would be expected at $\Delta T = 0$ if the droplet were incompressible.

However it is precisely at the critical point that the droplet-forming liquid becomes especially compressible, so the possibility exists that the pressure decrease resulting from $\Delta\mu$ increase might be accompanied by droplet expansion "to take up the slack." Accordingly, along the critical isotherm it is reasonable to anticipate bulk free energy varying with a higher power of $\Delta\mu$ than the first. Equation (106) with $\nu > 1$ permits inclusion of this possibility.

The specific expressions shown in Eqs. (105) and (106) are but the simplest of a variety of homogeneous functions of ΔT and $\Delta\mu$ that could be considered. Actually the critical-region exponent relations about to be derived are only sensitive to the degrees of homogeneity σ and ν , but not otherwise on the specific choice of functions.

In order to obtain the degree of the critical isotherm, substitute (105) and (106) for $\Delta T = 0$ into Eq. (103).

$$\begin{aligned} \rho(0, \Delta\mu) = & (\text{const}) \sum_{s=1}^{\infty} s^{(4/3)-\alpha_0} [(\Delta\mu)^\sigma + k_2' s^{-2/3}]^{11/6} \\ & \times \exp[-(\text{const}) (\Delta\mu)^\sigma s^{2/3} - (\text{const}) (\Delta\mu)^\nu s]. \end{aligned} \quad (107)$$

We later see that experimental critical-region measurements do not warrant consideration of ν larger than $3\sigma/2$, and for the range

$$1 \leq \nu \leq 3\sigma/2, \quad (108)$$

the last term in the exponent in Eq. (107) for small $\Delta\mu$ effectively provides an upper summation limit at $s = (\text{const}) (\Delta\mu)^{-\nu}$. Furthermore in the summation range we may take

$$[(\Delta\mu)^\sigma + k_2' s^{-2/3}] \cong k_2' s^{-2/3}. \quad (109)$$

³² In the strict sense, of course, this equation is not correct on account of its use for all $s \geq 1$ of the large- s asymptotic Z_s expression. However the error is substantially only an additive constant, and does not affect our subsequent predictions of changes in density with ΔT and $\Delta\mu$ which result strictly from rapid variations of the large- s tail of the sum shown.

³³ Signs have been chosen for constants in Eq. (105) so γ_∞ increases as gas density decreases. This is to be expected on the basis of any inhomogeneous-fluid theory such as utilized in Sec. III.

Therefore Eq. (107) may be approximated by

$$\begin{aligned} \rho(0, \Delta\mu) &\cong (\text{const}) \sum_{s=1}^{(\Delta\mu)^{-\nu}} s^{(1/9)-\alpha_0} \\ &= \rho_c - (\text{const}) \sum_{s=(\Delta\mu)^{-\nu}}^{\infty} s^{(1/9)-\alpha_0} \\ &= \rho_c - (\text{const}) (\Delta\mu)^{\nu[\alpha_0-(10/9)]} \\ &= \rho_c - (\text{const}) (\Delta\mu)^{2\nu\beta/3\sigma}. \end{aligned} \tag{110}$$

By virtue of the isothermal Gibbs–Duhem equation

$$\rho d\mu = dp, \tag{111}$$

we identify the critical isotherm exponent δ in

$$p_c - p \sim (\text{const}) (\rho_c - \rho)^\delta \tag{112}$$

as

$$\delta = 3\sigma/2\nu\beta. \tag{113}$$

A similar argument applies to deduction of the compressibility exponent γ' . On account of the Gibbs–Duhem equation again, it suffices to examine the isothermal derivative of ρ with respect to $\Delta\mu$, evaluated at $\Delta\mu=0$, since this should diverge at the critical point with the same inverse power of ΔT as the initial compressibility. Once again utilizing expressions (105) and (106) in Eq. (103), we find that the derivative has the following structure:

$$\begin{aligned} \left(\frac{\partial\rho(\Delta T, 0)}{\partial\Delta\mu}\right)_T &= (\text{const}) \sum_{s=1}^{\infty} s^{(4/3)-\alpha_0} \exp[-(\text{const}) (\Delta T)^\sigma s^{2/3}] \\ &\times \{ -(\text{const}) [(\Delta T)^\sigma + k_2'' s^{-2/3}]^{11/6} \\ &\times [(\text{const}) (\Delta T)^{\sigma-1} s^{2/3} + (\text{const}) (\Delta T)^{\nu-1} s] \\ &+ (\text{const}) (\Delta T)^{\sigma-1} [(\Delta T)^\sigma + k_2'' s^{-2/3}]^{5/6} \}. \end{aligned} \tag{114}$$

The exponential factor in the summand may now be reckoned as equivalent to an upper cutoff at $s = (\text{const}) (\Delta T)^{-3\sigma/2}$. The ν restriction, Eq. (108), thereupon permits selection of the dominant term in each square-bracketed binomial factor, so

$$\begin{aligned} \left(\frac{\partial\rho(\Delta T, 0)}{\partial\Delta\mu}\right)_T &\cong -(\text{const}) \sum_{s=1}^{(\Delta T)^{-3\sigma/2}} (\Delta T)^{\nu-1} s^{(10/9)-\alpha_0} \\ &+ (\text{const}) \sum_{s=1}^{(\Delta T)^{-3\sigma/2}} (\Delta T)^{\sigma-1} s^{(7/9)-\alpha_0}. \end{aligned} \tag{115}$$

For the ν range in Eq. (108), the negative first sum diverges, as ΔT goes to zero, more rapidly than the positive second sum. We may therefore disregard the second sum, and estimate the first by integration to obtain

$$\left[\frac{\partial\rho(\Delta T, 0)}{\partial\Delta\mu}\right]_T \cong -(\text{const}) (\Delta T)^{(3\sigma/2)[\alpha_0-(19/9)]+\nu-1}. \tag{116}$$

The exponent shown must be $-\gamma'$, so using Eq. (96) for α_0 , we have found

$$\gamma' = \frac{3}{2}\sigma - \beta - \nu + 1. \tag{117}$$

It may be shown³⁰ from the general fluctuation–compressibility theorem that the two exponents ν' and η appearing in the pair correlation function asymptote (97) are related to γ' by the equation

$$\eta = 2 - (\gamma'/\nu'). \tag{118}$$

Our ν' and γ' results (102) and (117) lead then to

$$\eta = (2/\sigma) (\beta + \nu - 1) - 1. \tag{119}$$

The main results of this paper are Eqs. (102), (113), (117), and (119) expressing ν' , δ , γ' , and η in terms of the phenomenological surface tension and coexistence curve exponents, and the parameter ν . If the value $\sigma=1.29$ of Ref. 29 is accepted, then the predicted ν' is in perfect accord with the three-dimensional Ising model prediction quoted in Eq. (56). Although the ν uncertainty generates sets of predictions for the other indices, depending on the particular value selected for this parameter, we stress that such a choice produces satisfactory agreement with the presently rather poorly defined experimental results for condensing fluids. If β is taken to be $\frac{1}{3}$, then the choice $\nu=1.35$ yields the following predictions:

$$\delta = 4.30, \quad \gamma' = 1.25, \quad \eta = 0.059. \tag{120}$$

The first of these straddles the value 4.4 measured for Xe by Habgood and Schneider,³⁴ and the value 4.2 claimed for CO₂ by Widom and Rice.³⁵ The latter two agree with values proposed for the Ising model.²³

VIII. DISCUSSION

We have just seen that our physical-cluster-theory critical-exponent predictions can fit the behavior of three-dimensional gases reasonably well. However the “scaling-law” approach^{14,15} provides another scheme in which the classical fluid exponents may be accommodated. Indeed the “scaling laws” provide in some ways a more powerful tool than the present theory, since they encompass the entire critical region (rather than just the vapor side of the coexistence zone), as well as produce predictions for specific heats which cannot be done in an obvious way with our physical cluster theory. Nevertheless, an interesting relation may be established between the two approaches, starting from one of the deductions of the “scaling laws”^{14,15}:

$$\gamma' = \beta(\delta - 1). \tag{121}$$

Substituting our ν -dependent γ' and δ results, we find that

$$(3\sigma/2) + 1 - \nu = 3\sigma/2\nu. \tag{122}$$

³⁴ H. W. Habgood and W. G. Schneider, *Can. J. Chem.* **32**, 98 (1954).

³⁵ B. Widom and O. K. Rice, *J. Chem. Phys.* **23**, 1250 (1955).

The two roots of this quadratic equation in ν are 1 and $3\sigma/2$, precisely the endpoints of the interval shown in Eq. (108). Therefore we may say that special scaling laws can occur in physical-cluster theory as isolated cases, but generally they are not implied.

It should be stressed that the present theory is intended to apply only to classical continuum fluids, and makes no pretense at direct prediction of critical properties for the theoretically convenient, but unrealistic Ising-model lattice gases. We have assumed of course spherical-droplet shape to be the mechanically stable form at all temperatures, but with lattice gases on a cubical lattice for example, surface tension must be expected to depend on direction in such a way as to produce cubical "droplets." Even if it is valid to assume hydrodynamics applies to the lattice fluid so as to provide surface normal modes analogous to the ones considered here, the low-frequency spectrum should be strongly affected by droplet shape.³⁶ In addition we remark that the critical points investigated for lattice gases invariably occur for half-filled lattices regardless of interaction range, whereas the critical point for a lattice-gas model, which actually corresponds to a real fluid as the model potential range increases indefinitely (so as to "wash out" the lattice granularity), occurs asymptotically at zero density on a per-lattice-site basis; there is no *a priori* reason to expect identical exponents for these distinct critical points.

Essam and Fisher^{6,7} have proposed an alternative physical cluster theory which is strongly motivated by lattice-gas considerations. Both the implementation and results of their work differ from that reported here, yielding in fact a scaling law. The fundamental differences between the two versions are

(a) Essam and Fisher disregard cluster excluded volume (or "interference"), whereas we have accounted for it through the cavity free energies W_s ;

(b) Droplet surface tension vanishes linearly with ΔT in the Essam-Fisher formalism, whereas we have retained the $(\Delta T)^\sigma$ power law required phenomenologically;

(c) No discontinuous jump in the power of s entering into the large- s cluster partition function occurs in the Essam-Fisher theory, as it does in the present development;

(d) Essam and Fisher permit the possibility that surface free energy of droplets might asymptotically vary as some power of s other than $\frac{3}{2}$, but we do not.

It will perhaps eventually develop that these alternative approaches are not so much in conflict if their respective domains of applicability, lattice gases, and continuum fluids are not construed as overlapping.

If one is willing to reach outside the present cluster theory's domain, the three independent input indices

³⁶ It may happen that the lattice-gas surface tension becomes isotropic at the critical point, so as to permit in that limit spherical droplets. However the rate of attainment of isotropy would be decisive in determining whether or not the continuum approach used in this paper would apply.

σ , β , and ν may be related to one another. For example, Eq. (46) displays the surface-tension index required by the Cahn-Hilliard inhomogeneous fluid theory:

$$\sigma = \frac{1}{2}\gamma' + 2\beta. \quad (123)$$

By inserting our result (117) for γ' , the unmeasurable cluster expansivity index ν may be expressed in terms of σ and β :

$$\nu = 3\beta - \frac{1}{2}\sigma + 1. \quad (124)$$

In addition Stell³⁷ has obtained a relation between η and δ from a functional Taylor-expansion theory of the molecular correlation function with a truncation that should be suitable in the critical region:

$$\eta = 2 - 3(\delta - 1)/(\delta + 1). \quad (125)$$

If our η and δ results are inserted here, and ν eliminated by Eq. (124), a quadratic equation for σ is obtained with coefficients depending on β :

$$\left(\frac{3}{2} - \frac{7}{2}\beta\right)\sigma^2 + (25\beta^2 - 5\beta)\sigma - 24\beta^3 - 8\beta^2 = 0. \quad (126)$$

The appropriate solution is

$$\sigma = [\beta/(3 - 7\beta)] [(289\beta^2 - 218\beta + 73)^{1/2} - 25\beta + 5]. \quad (127)$$

The value of σ corresponding to $\beta = \frac{1}{2}$ in this expression is 1.18, only in fair agreement with the experimental value 1.29.²⁹ However the predicted σ is very sensitive to β in this range, and a slight increase in β to 0.384 will reproduce the experimental σ . One hopes of course that yet another exponent relation will be eventually uncovered so that even the remaining single free exponent could be predicted!

As a final matter we recall that the droplet oscillation spectrum (58) used in this paper is strictly speaking appropriate only to incompressible liquids. Although the incompressibility assumption must surely be accurate at low temperature, one might easily question its validity in the critical region where droplets are very spongy. The result of the more complex hydrodynamic problem with finite compressibility reveals a balance between vanishing surface tension γ_∞ and the diverging adiabatic compressibility κ_s . Since the product $\gamma_\infty\kappa_s$ however still vanishes at T_c, μ_c , the spectrum (58) is automatically recovered in this more general calculation, and one is indeed justified in disregarding cluster compressibility in the critical region.

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APPENDIX A

We consider a vessel in a gravitational field g , filled with a sufficient number of molecules so as to exhibit coexisting liquid and vapor. Let the z axis of a Cartesian

³⁷ G. Stell, Preprint.

coordinate system point "upward," i.e., out of the liquid phase and into the vapor. It will be presumed that g is sufficiently weak that density variations within the bulk phases due to hydrostatic compression are negligible. Let $\rho^{(1)}(\mathbf{r}_1)$ and $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ be the molecular distribution functions in the inhomogeneous fluid system.

Next consider application of a weak sinusoidal external field to the system, of the form

$$u(\mathbf{r}) = \xi \sin(\mathbf{q} \cdot \mathbf{r}), \tag{A1}$$

so that the system of N molecules receives an increment

$$\chi(\mathbf{q}, z_1) = (kT)^{-1} \left\{ \rho^{(1)}(\mathbf{r}_1) + \int_V [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] \cos(\mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{r}_2 \right\}. \tag{A4}$$

The amount of reversible isothermal work done on the system in applying external potential u is

$$-\frac{1}{4} V \xi^2 \langle \chi(\mathbf{q}, z_1) \rangle, \tag{A5}$$

involving the spatial average of the susceptibility

$$\langle \chi(\mathbf{q}, z_1) \rangle = V^{-1} \int_V \chi(\mathbf{q}, z_1) d\mathbf{r}_1. \tag{A6}$$

If our vessel were filled with just an homogeneous vapor phase (v), the susceptibility function would be independent of height z_1 , and would be given by a simplified version of (A4) appropriate to the isotropic homogeneous phase:

$$\chi_v(\mathbf{q}) = (kT)^{-1} \times \left\{ \rho_v + \int_V [\rho_v^{(2)}(\mathbf{r}_{12}) - (\rho_v)^2] \cos(\mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{r}_{12} \right\}, \tag{A7}$$

in which ρ_v is the uniform density and $\rho_v^{(2)}(\mathbf{r}_{12})$ the radial distribution function. Obviously a similar expression obtains for $\chi_l(\mathbf{q})$, the homogeneous liquid-phase susceptibility. Analogous to Result (A5) furthermore, the reversible isothermal works that $u(\mathbf{r})$ would perform on the systems containing just homogeneous vapor or liquid would be respectively:

$$-\frac{1}{4} V \xi^2 \chi_v(\mathbf{q}) \quad \text{and} \quad -\frac{1}{4} V \xi^2 \chi_l(\mathbf{q}). \tag{A8}$$

Following Gibbs' approach³⁸ to the study of equilibrium interfacial phenomena, introduce an equimolar dividing surface in the inhomogeneous system at height z_0 , parallel to the interface. Denote by V_v and V_l the volumes above and below this mathematical

of potential energy

$$\sum_{i=1}^N u(\mathbf{r}_i) = \xi \sum_{i=1}^N \sin(\mathbf{q} \cdot \mathbf{r}_i). \tag{A2}$$

We will allow only \mathbf{q} 's parallel to the interface, so $q_x = 0$.

It is a straightforward matter to calculate the density variation linear in ξ induced by $u(\mathbf{r})$; the new singlet density is

$$\rho^{(1)}(\mathbf{r}_1) - \chi(\mathbf{q}, z_1) u(\mathbf{r}_1), \tag{A3}$$

where the position-dependent susceptibility $\chi(\mathbf{q}, z_1)$ is

dividing surface, respectively, the vapor- and liquid-phase volumes. The standard subtractive procedure then identifies the superficial excess susceptibility $\chi^{(s)}(\mathbf{q})$ for the surface region by setting

$$V \langle \chi(\mathbf{q}, z_1) \rangle - V_v \chi_v(\mathbf{q}) - V_l \chi_l(\mathbf{q}) = S \chi^{(s)}(\mathbf{q}), \tag{A9}$$

for interfacial area S . By utilizing (A4) and (A7), we now obtain a pair-distribution-function integral expression for the interfacial susceptibility:

$$\begin{aligned} \chi^{(s)}(\mathbf{q}) = & (kT)^{-1} \int_{-\infty}^{+\infty} dz_1 \int d\mathbf{r}_{12} \cos(\mathbf{q} \cdot \mathbf{r}_{12}) \\ & \times \{ \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - U(z_1 - z_0) \rho_v^{(2)}(\mathbf{r}_{12}) \\ & - [1 - U(z_1 - z_0)] \rho_l^{(2)}(\mathbf{r}_{12}) - \rho^{(1)}(z_1) \rho^{(1)}(z_2) \\ & + U(z_1 - z_0) (\rho_v)^2 + [1 - U(z_1 - z_0)] (\rho_l)^2 \}, \end{aligned} \tag{A10}$$

where $U(z)$ is the unit step function. We have here presumed that the system is sufficiently large, and the contribution to $\chi^{(s)}$ sufficiently well localized around the interfacial zone, that the spatial integrals could be taken between infinite limits.

Consider now the dynamical quantity

$$S(\mathbf{q}) = \sum_{i=1}^N \sin(\mathbf{q} \cdot \mathbf{r}_i), \tag{A11}$$

proportional to potential energy (A2). In the absence of external potential $u(\mathbf{r})$, the mean expectation value of S , $\langle S \rangle$, will vanish due to translation invariance parallel to the interface. However by direct calculation in the canonical ensemble one establishes that

$$\begin{aligned} \langle S^2(\mathbf{q}) \rangle = & \frac{1}{2} \int_V d\mathbf{r}_1 \left\{ \rho^{(1)}(\mathbf{r}_1) + \int_V d\mathbf{r}_2 [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] \cos(\mathbf{q} \cdot \mathbf{r}_{12}) \right\} \\ = & \frac{1}{2} V kT \langle \chi(\mathbf{q}, z_1) \rangle. \end{aligned} \tag{A12}$$

Again, $\langle S^2 \rangle$ for either pure vapor or liquid could similarly have been written in terms of the bulk-phase susceptibilities χ_v or χ_l . Consequently the procedure of subtracting bulk-phase contributions results in a

³⁸ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 339.

surface-zone fluctuation-susceptibility theorem:

$$\langle S^2(\mathbf{q}) \rangle^{(s)} \equiv \langle S^2(\mathbf{q}) \rangle - \frac{1}{2}(kT) [V_s \chi_v(\mathbf{q}) + V \alpha_l(\mathbf{q})] = \frac{1}{2} kT S \chi^{(s)}(\mathbf{q}). \tag{A13}$$

It was one of the major points of Refs. 10 and 12 that an elementary assessment of surface fluctuations in terms of surface waves and an intrinsic surface tension γ_0 could be carried out with valuable physical implications. Classical energy equipartition among the independent surface modes in this method leads directly to the evaluation of $\langle S^2(\mathbf{q}) \rangle^{(s)}$, and in turn one obtains the surface susceptibility

$$\chi^{(s)}(\mathbf{q}) = \{(\rho_l - \rho_v)^2 / [m_0 g(\rho_l - \rho_v) + \gamma_0 q^2]\}. \tag{A14}$$

We remark here that since the quantity

$$-\frac{1}{4} V \xi^2 \chi^{(s)}(\mathbf{q}), \tag{A15}$$

analogous to (A5) and (A8), must represent the excess surface zone contribution to isothermal reversible work done on the system by $u(\mathbf{r})$, $\chi^{(s)}(\mathbf{q})$ as shown in (A14) can equally well be established by calculating the sinusoidal dimpling effect of $u(\mathbf{r})$ on the liquid surface.

The important point to make now is that expression (A14) is the surface analog of the Ornstein-Zernike bulk phase susceptibility (i.e., pair-correlation-function Fourier transform). Since the quadratic-denominator behavior of the latter is known to be deficient in the critical region, the strong implication exists that the former should require revision. Arguing by this analogy, the effective surface tension appearing in a $\chi^{(s)}$ denominator in the double limit $g \rightarrow 0$, $T \rightarrow T_c$ should exhibit a fractional-power behavior as a function of \mathbf{q} , thereby providing "nonclassical" critical-point surface phenomena.

Although we cannot immediately identify this wavelength-dependent effective surface tension with the quantity $\gamma_2 q(x)$ for the same wavelength appearing in our cluster theory, it seems likely that a quantitative connection could be made through consideration of the average extent of local surface "tipping" from the horizontal in the sequential-mode addition procedure.

APPENDIX B

We now sketch the two-dimensional version of the physical cluster theory, with the sequential-mode addition procedure. As before, the central problem consists in evaluation of the s -particle cluster partition function, which in two dimensions will adopt the form

$$\exp\left(\frac{s\mu}{kT}\right) Z_s(T, \mu) \sim (\text{const}) A s^{1-\alpha_0} \left[\prod_{i=1}^{t_2} \frac{kT}{\hbar \bar{\omega}_i} \right] \times \exp\{-[a(\Delta T, \Delta\mu) - \mu]s + 2(\pi b_0)^{1/2} \gamma_\infty s^{1/2}\} (kT)^{-1}. \tag{B1}$$

A stands here for the area of the two-dimensional vessel. γ_∞ must now be interpreted as a line tension at the boundary of the essentially circular cluster, and b_0

is the area per molecule in the dense cluster-forming fluid.

In this two-dimensional sequel, the analog of surface tension curvature corrections (which gave $s^{1/3}$ free-energy contributions in three dimensions) are only of order s^0 . Since they do not formally dominate $\ln s$ terms as before, there is no need to redo the crude density-profile calculation of Sec. III to justify their neglect.

The main issue concerns the vibration frequencies $\bar{\omega}_i$ of the two-dimensional droplets. Figure 8 shows a droplet, with undistorted radius R , whose distortion may be described by radius

$$r(\theta) = R + w(\theta). \tag{B2}$$

Let the flow for oscillatory motion of the droplet under the influence of its boundary tension be described by flow potential $\psi(r, \theta, t)$, satisfying the two-dimensional Laplace equation

$$\nabla^2 \psi = 0. \tag{B3}$$

We can reasonably anticipate that individual modes of oscillation will correspond to separate circular harmonics, with

$$\psi(r, \theta, t) = A' \exp[i\bar{\omega}_s(l)t] \begin{Bmatrix} \sin(l\theta) \\ \cos(l\theta) \end{Bmatrix} r^l. \tag{B4}$$

The eigenfrequencies $\bar{\omega}_s(l)$ are determined by the boundary condition on ψ at the droplet's edge. One may easily adapt the corresponding three-dimensional development³⁹ to two dimensions to conclude that ψ must satisfy

$$\frac{m_0}{b_0} \frac{\partial^2 \psi}{\partial t^2} - \frac{\gamma_2 q_s(l/l_{\max})}{R^2} \frac{\partial}{\partial r} \left(\psi + \frac{\partial^2 \psi}{\partial \theta^2} \right) = 0 \tag{B5}$$

at $r=R$. Here we have utilized $\gamma_2 q_s(l/l_{\max})$ as the appropriate boundary tension provided as in the three-dimensional case by a self-consistent sequential mode addition procedure. Substituting (B4) into Boundary

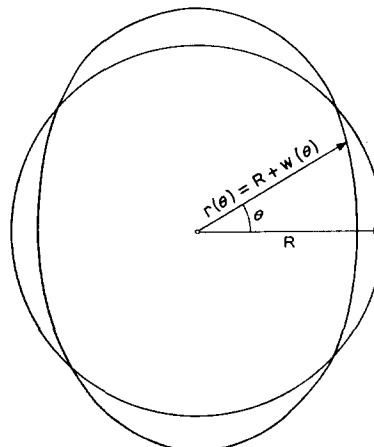


FIG. 8. Two-dimensional droplet distortion. R is the radius of the circular undistorted droplet, and $w(\theta)$ measures the radial distortion for varying angle.

³⁹ L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley Publishing Co., Reading, Mass., 1959), p. 239.

Condition (B5) yields the following spectrum:

$$[\bar{\omega}_s(l)]^2 = \frac{\pi^{3/2}\gamma_2 q_s(l/l_{\max}) l(l-1)(l+1)}{m_0 b_0^{1/2} s^{3/2}}; \quad (B6)$$

in obtaining this result we have used the obvious identity $\pi R^2 = b_0 s$. For given l the frequencies are doubly degenerate, corresponding to independence of the sine and cosine solutions in (B4), and an upper cutoff $l_{\max} \cong \alpha s^{1/2}$ must be applied.

The condition of self-consistency which determines

$$q_s(x) = 1 + \frac{\alpha k T}{(4\pi b_0 s)^{1/2} \gamma_2} (1-x) \ln \left\{ \frac{\hbar^2 \pi^{3/2} \gamma_2}{k^2 T^2 m_0 b_0^{1/2}} \right\} + \frac{k T}{(4\pi b_0 s)^{1/2} \gamma_2} \left\{ \Delta(s, l) + \int_{l+1/2}^{\alpha s^{1/2} + 1/2} dl' \ln \left[\frac{l'(l'-1)(l'+1)}{s^{3/2}} \right] \right\} + \frac{k T}{(4\pi b_0 s)^{1/2} \gamma_2} \sum_{l'=l+1}^{l_{\max}} \ln q_s \left(\frac{l'}{l_{\max}} \right), \quad (B8)$$

where

$$\Delta(s, l) = \sum_{l'=l+1}^{l_{\max}} \ln \left[\frac{l'(l'-1)(l'+1)}{s^{3/2}} \right] - \int_{l+1/2}^{\alpha s^{1/2} + 1/2} dl' \ln \left[\frac{l'(l'-1)(l'+1)}{s^{3/2}} \right]. \quad (B9)$$

The infinite- s limit of q_s , denoted as before by q , now satisfies

$$q(x) = 1 + A_2 T \times \left[\ln(D_2 T^2) (x-1) - \frac{3}{2} x \ln x + \int_x^1 \ln q(y) dy \right]; \quad (B10)$$

$$A_2 = \frac{\alpha k}{(4\pi b_0)^{1/2} \gamma_2}, \quad D_2 = \frac{k^2 m_0 b_0^{1/2} e^{3/2}}{\hbar^2 \pi^{3/2} \gamma_2 \alpha^{3/2}}.$$

From this equation one verifies that for all $T < T_c$, $q(x)$ possesses the following small- x development

$$q(x, T) \sim q(0, T) - Q_1(T) x \ln x + Q_2(T) x; \quad (B11)$$

$$q(0, T) = 1 + A_2 T \left[-\ln(D_2 T^2) + \int_0^1 \ln q(y, T) dy \right],$$

$$Q_1(T) = \frac{3}{2} A_2 T,$$

$$Q_2(T) = A_2 T \ln[D_2 T / q(0, T)].$$

The leading x dependence near $x=0$ is now linear (to the nearest power of x) rather than quadratic as in three dimensions, so the wavelength dependence or dispersion is relatively more pronounced. At T_c , the small- x development shifts to

$$q(x, T_c) \sim -\frac{5}{2} A_2 T_c x \ln x - A_2 T_c x \ln \ln(1/x) + O(x). \quad (B12)$$

The deduction of the Z_s asymptote proceeds substantially as before from the q_s functional equation, except that now $\Delta(s, l)$ gives rise to no lns contributions. One finally obtains, below T_c ,

$$Z_s(T, \mu) \sim (\text{const}) A s^{-8-\alpha_0} \times \exp\{-[a(T, \mu)s + (4\pi b_0)^{1/2} \gamma_\infty s^{1/2}](kT)^{-1}\}, \quad (B13)$$

whereas the correct large- s asymptote at the critical point is

$$Z_s(T_c, \mu_c) \sim (\text{const}) A s^{-(35/4)-\alpha_0} \exp[-a(T_c, \mu_c)s/kT]. \quad (B14)$$

the two-dimensional line tension $\gamma_2 q_s(l/l_{\max})$ is an obvious analog of Eq. (69) in the text:

$$\exp \left[\frac{-\gamma_2 q_s(l/l_{\max}) (4\pi b_0 s)^{1/2}}{kT} \right] = \left\{ \prod_{l'=l+1}^{l_{\max}} \left[\frac{kT}{\hbar \bar{\omega}_s(l')} \right]^2 \right\} \exp \left[\frac{-\gamma_2 (4\pi b_0 s)^{1/2}}{kT} \right]. \quad (B7)$$

If we take logarithms in this equation, and set $x=l/l_{\max}$, the determining equation for q_s becomes

These two expressions may be interpolated along the coexistence curve by

$$\exp(s\mu_{\text{sat}}/kT) Z_s(T, \mu_{\text{sat}}) \sim (\text{const}) A s^{-8-\alpha_0} [\gamma_\infty(T) + k_2 s^{-1/2}]^{3/2} \times \exp[-(4\pi b_0)^{1/2} \gamma_\infty(T) s^{1/2}/kT]. \quad (B15)$$

The previous stragem of selecting α_0 so as to reproduce a given coexistence-curve index β gives

$$\alpha_0 = (\beta/2\sigma) - (27/4), \quad (B16)$$

where σ is the index for line tension γ_∞ .

The identification of the correlation range exponent ν' in terms of σ may be implemented by the means used at the beginning of Sec. VII. However now the common structure factor is size-scaled as $S(s^{-1/2}\nu)$. The result finally is that

$$\nu' = \sigma. \quad (B17)$$

The line tension and cluster-bulk-free-energy interpolations, in terms of the simple homogeneous forms (105) and (106), may be carried over to the two-dimensional regime without change. Then when ν is confined to the range

$$1 \leq \nu \leq 2\sigma, \quad (B18)$$

the previous manipulations in Sec. VII may readily be adapted to give

$$\delta = 2\sigma/\nu\beta, \quad \gamma' = 2\sigma - \beta - \nu + 1, \quad \eta = (1/\sigma)(\beta + \nu - 1). \quad (B19)$$

Although (B17) appears to be exactly satisfied by the two-dimensional Ising models (both ν' and σ are unity⁴⁰), no single ν value will yield the accepted δ , γ' , and η values for these models (with $\beta = \frac{1}{8}$). However in view of the comments in Sec. VIII, this fact need not be viewed with alarm.

⁴⁰ C. Domb, Advan. Phys. 9, 196 (1960).