

Comment on the Translation-Rotation Paradox in the Theory of Irreversible Condensation

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In two recent papers^{1,2} in this Journal devoted to the basis of classical nucleation theory, a controversy has arisen concerning the appropriate form of the distribution function of matter among physical clusters. In the first of these, Lothe and Pound¹ have advocated explicit consideration of rotational degrees of freedom of the cluster droplet as a whole. They have accordingly produced cluster distributions that give nucleation rates typically in excess of the older Becker-Doering³ and Zeldovich⁴ results by a factor of 10^{17} , and are thus in disagreement with measured critical supersaturation ratios. However Reiss and Katz² have challenged the approach in Ref. 1, and have provided an evaluation of the physical cluster distribution which substantially confirms the older theory, and so restores agreement between theory and experiment.

It is our purpose to remark that the theory of physical clusters that has just been developed to describe static critical phenomena⁵ displays as a byproduct an essential confirmation of the Reiss and Katz cluster distribution. We stress that the logical structure of this critical phenomena theory is entirely independent of that propounded by Reiss and Katz.

Various results for physical cluster distributions may be classified by their behavior for large i , the number of molecules contained within the cluster. For present purposes it suffices to write the following generic form

for the density n_i of i molecule clusters in the equilibrium vapor phase at temperature T (less than the critical T_c),

$$n_i \sim C i^{-q} \exp[-W(i)/kT].$$

C is a positive constant, k is Boltzmann's constant, and the various theories agree that $W(i)$ is a cluster Gibbs free energy consisting of bulk and surface terms; specifically, $W(i)$ may be written thus,⁶

$$W(i) = (\mu_l - \mu) i + (6\pi^{1/2} v_l)^{2/3} \gamma(T) i^{2/3},$$

where μ_l and v_l are the liquid phase chemical potential and molecular volume, γ is the surface tension, and μ is the ambient vapor-phase chemical potential.

The theories of n_i differ primarily in assignment of exponent q . For compact spherical clusters, the moments of inertia are easily found to vary as $i^{5/3}$ for large i , and so the prescription outlined by Lothe and Pound leads in turn to a q value of $-7/2$. On the other hand Reiss and Katz conclude that q should be $+1$.

The relevant aspect of the critical-point investigation reported in Ref. 5 is an expression for q in terms of the critical indices β and σ for vanishing of the liquid-vapor density difference and of surface tension, respectively, at T_c .⁷ One finds

$$q = (2\beta/3\sigma) + 7/9.$$

An adequate representation of liquid-vapor coexistence consists in taking β as $1/3$,⁸ and the most accurate surface tension measurements indicate σ is 1.29.⁹ Therefore one calculates q to be 0.95, in substantially complete agreement with Reiss and Katz, but in clear contradiction to the Lothe-Pound result.

¹ J. Lothe and G. M. Pound, J. Chem. Phys. **36**, 2080 (1962).

² H. Reiss and J. L. Katz, J. Chem. Phys. **46**, 2496 (1967).

³ R. Becker and W. Doering, Ann. Physik **24**, 719 (1935).

⁴ J. Zeldovich, Soviet Phys.—JETP **12**, 525 (1942).

⁵ F. H. Stillinger, J. Chem. Phys. **47**, 2513 (1967).

⁶ Surface-tension curvature corrections could be considered, but are irrelevant for our main conclusion; see F. P. Buff and J. G. Kirkwood, J. Chem. Phys. **18**, 991 (1950); F. P. Buff, *ibid.* **23**, 419 (1955).

⁷ L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967), Sec. V.

⁸ E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945).

⁹ R. A. Lovett and F. P. Buff, "The Surface Tension of Simple Fluids," in *Simple Dense Fluids; Data and Theory*, Z. W. Salsburg and H. L. Frisch, Eds. (Academic Press Inc., New York, to be published).