

# On a Reconsideration of Classical Nucleation Theory

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A correct account of the collective motion of a cluster does not require the Lothe-Pound correction; furthermore, this correction is shown to contradict the laws of thermodynamics.

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The main point of the recent discussion of the Lothe-Pound reconsideration of the classical theory of homogeneous nucleation<sup>(1,2)</sup> deals with the contribution of extra degrees of the freedom of the cluster to the Gibbs free energy of its formation. The account of this contribution made by Lothe and Pound<sup>(1)</sup> gave rise to an increase in the equilibrium concentration of the clusters of about  $10^{17}$  times (for water vapor). It will be shown here that the exact account of the cluster collective motion is contained in classical theory. For simplicity, we shall consider only the cluster translational motion.

The cluster equilibrium concentration can be expressed as

$$N_g = N_1^g Z_g / Z_1^g \quad (1)$$

where

$$Z_g = Z_g^{(\text{conf})} \int \dots \int d^{3g} p \exp \left\{ -\frac{\beta}{2m} \sum_i p_i^2 \right\} = Z_g^{(\text{conf})} Z_g^{(\text{mom})} \quad (2)$$

is the cluster partition function and

$$Z_1^g = \frac{V^g}{h^{3g}} \left( \int d^3 p \exp \left\{ -\frac{\beta}{2m} p^2 \right\} \right)^g \quad (3)$$

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is the partition function for  $g$  noninteracting vapor molecules. Here,  $V$  is volume of entire system. It is assumed that the temperatures of clusters and of ambient are the same, i.e., the nucleation process is isothermal. The Lothe–Pound correction arose from replacing the term  $\int d^3p \exp\{-\beta p^2/2m\}$  in the momentum part of the partition function (2) by the term  $\int d^3P \exp\{-\beta P^2/2mg\}$  to take account of a cluster translation with the momentum  $\mathbf{P} = \sum_i \mathbf{p}_i$ . We shall demonstrate that the correct inclusion of this effect is contained in the classical theory result. Actually, the momentum part of the partition function of a cluster with a collective translation velocity  $\mathbf{P}/mg$  is

$$Z_{\text{cl}}^{(\text{mom})} = \int d^3P \exp\left\{-\frac{\beta P^2}{2mg}\right\} \int \cdots \int_{\sum_i^g \mathbf{p}_i = \mathbf{P}} d^{3g}p \exp\left\{-\beta \sum_i^g \frac{\mathbf{p}_i - \mathbf{P}/g}{2m}\right\} \quad (4)$$

Here, the restriction  $\sum_i^g \mathbf{p}_i = \mathbf{P}$  imposed on the integration area provides conservation of the total number of independent variables. Thus, integration over  $\mathbf{P}$  may not be performed independently, and the separation of the part corresponding to the collective translation in the cluster's partition function as was made by Abraham and Pound,<sup>(3)</sup> (Eqs. 14, 23) is erroneous.

The integration over  $\{\mathbf{p}_i\}$  in (4) may be performed without restriction on the integration area by introducing into the integrand the  $\delta$ -function  $\delta(\sum_i^g \mathbf{p}_i - \mathbf{P})$ . Then,

$$Z_{\text{cl}}^{(\text{mom})} = \int d^3P \exp\left\{-\frac{\beta P^2}{2mg}\right\} \int \cdots \int d^{3g}p \delta\left(\sum_i^g \mathbf{p}_i - \mathbf{P}\right) \exp\left\{-\frac{\beta}{2m} \sum_i^g \left(\mathbf{p}_i - \frac{\mathbf{P}}{g}\right)^2\right\} \quad (5)$$

or, integrating first over  $\mathbf{P}$  with this  $\delta$ -function, we obtain

$$\begin{aligned} Z_{\text{cl}}^{(\text{mom})} &= \int \cdots \int d^{3g}p \exp\left\{-\frac{\beta}{2mg} \left(\sum_i^g \mathbf{p}_i\right)^2 - \frac{\beta}{2m} \sum_i^g \left(\mathbf{p}_i - \frac{1}{g} \sum_j^g \mathbf{p}_j\right)^2\right\} \\ &= \int \cdots \int d^{3g}p \exp\left\{-\frac{\beta}{2m} \sum_i^g p_i^2\right\} = Z_g^{(\text{mom})} \end{aligned} \quad (6)$$

Thus, we have proved that taking account of the translational motion of a cluster in the form (4) does not change its partition function (2). Any other of the cluster's collective degrees of freedom (rotation, density fluctuation, etc.) may be considered in the same way. Obviously, they also have no influence on the final result of the classical theory.

The same result was obtained by Reiss *et al.*,<sup>(2)</sup> but they did not introduce the center-of-mass momentum, which is why the result was not crucial for the supporters of Lothe–Pound correction.

The momentum parts of the partition functions (2) and (3) are the same and must be cancelled out in Eq. (1). Only the magnitudes of configurational integrals determine the equilibrium cluster concentration.

The purpose of our consideration was to clear up the errors concerned with introducing the Lothe–Pound correction. Furthermore, their revision of the classical

theory can be rejected on the basis of the following quite general argument. It appears that the Lothe–Pound result not only gives rise to the striking overestimation of the cluster equilibrium concentration, but also implies that the vapor pressure over the droplet engaged in a thermal motion must be higher than that predicted by the Kelvin–Gibbs formulas for the resting droplet. Then, there must be an isothermal distillation from a droplet at rest to a moving one. However, that would be a transition of a substance to a higher energy state without external energy supply, which would be in contradiction with the laws of thermodynamics.

## REFERENCES

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