

1 Translation-rotation correction factor in the theory of homogeneous 2 nucleation

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8 An analytical formula for the correction factor which is to multiply the classical expression for the
 9 nucleation rate to account the translation and rotation of the critical nucleus is proposed. The
 10 formula is based on the Reiss approach considering the contribution from the clusters translational
 11 degrees of freedom, Frenkel's kinetic theory of liquids, and Kusaka's theory. Using this formula we
 12 determined the correction factor for argon vapor-to-liquid phase nucleation for the temperature
 13 range 80–110 K. These evaluations are in a good agreement with the correction factor calculated
 14 numerically by Kusaka (2006). Basing on the Gibbs theory of capillarity it is also shown that for the
 15 case of ideal gas-to-liquid nucleation the exponent in the classical formula for the rate of nucleation
 16 is strictly equal to the reversible work of drop formation. © 2009 American Institute of Physics.
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19 I. INTRODUCTION

20 In the theory of nucleation from the vapor phase it is
 21 important to know the equilibrium cluster size distribution.
 22 On the other hand, the nucleation rate is proportional to the
 23 concentration of critical nuclei. This concentration is, in turn,
 24 related to the reversible work of formation of the critical
 25 cluster (nucleus). More than half a century ago Frenkel¹ and
 26 then Kuhrt^{2,3} noted that the contribution to the free energy of
 27 the critical nucleus from the translational and rotational de-
 28 grees of freedom should be accounted when calculating the
 29 cluster size distribution. Due to this contribution the so-
 30 called free energy correction factor arises in the formula for
 31 the nucleation rate. Lothe and Pound⁴ estimated (within the
 32 framework of the Gibbs imaginary process of drop forma-
 33 tion) the translational-rotational contribution to the free en-
 34 ergy of critical nucleus which gave the correction factor of
 35 about 10^{17} . Reiss and co-workers^{5,6} argued that the Lothe
 36 and Pound correction factor was exaggerated too much due
 37 to the neglect of the fluctuation of the center of mass of the
 38 nucleus and a new correction was proposed to be a factor of
 39 10^3 – 10^6 . Later on Reiss *et al.*⁷ developed another approach
 40 which gave the correction factor for water of about 10^4 . Par-
 41 tially the discrepancy between the Reiss correction and that
 42 of Lothe and Pound is related to different interpretations of
 43 the classical formula for the reversible work of formation of
 44 the critical nucleus⁸ and not only to the different level of
 45 mathematical rigor. Recently Kusaka⁸ derived a rigorous for-
 46 mula for the correction factor within the framework of the
 47 Gibbs process of drop formation and calculated numerically
 48 this factor for the Lennard-Jones system. The calculated val-
 49 ues ranged from 10^9 to 10^{13} which were considerably higher
 50 than the Reiss correction factor and less essentially than the
 51 Lothe–Pound one.

The numerical calculation is probably the most direct 52
 way to determine the correction factor. However, the calcu- 53
 lations of this kind are only possible for simple systems and, 54
 therefore, an analytical expression for the correction factor 55
 applicable to a wide range of real systems is still necessary. 56
 In this paper we propose such an analytical formula and 57
 evaluate the correction factor for the Lennard-Jones system 58
 to compare with Kusaka's numerical simulation results.⁸ 59

II. TRANSLATIONAL-ROTATIONAL CONTRIBUTIONS 60 TO THE CLUSTER FREE ENERGY 61

Frenkel¹ was the first to point out that the translational 62
 and rotational degrees of freedom should be accounted when 63
 evaluating the partition function of the cluster (drop). To de- 64
 termine the equilibrium cluster size distribution, Frenkel 65
 considered an ensemble of clusters as an ideal gas mixture. 66
 In this case a statistical mechanical analysis gives^{1,7} 67

$$N_n = \left(\frac{N_1}{q_1} \right)^n q_n = q_n e^{\mu_v n / k_B T}, \quad (1) \quad 68$$

where N_n is the equilibrium number of n -sized clusters (con- 69
 sisting of n monomeric molecules), N_1 is the number of 70
 monomers in the vapor, q_1 and q_n are the partition functions 71
 within the canonical ensemble for monomer and n -mer, re- 72
 spectively, μ_v is the chemical potential for the vapor mol- 73
 ecules, k_B is the Boltzmann constant, and T is the absolute 74
 temperature of the system. The right Eq. (1) follows upon 75
 recognition of the standard form for the chemical potential of 76
 an ideal gas.⁷ 77

The partition function of the n -sized cluster may be writ- 78
 ten as¹ 79

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$$q_n = \sum_i e^{-H_{ni}/k_B T} = e^{-f_n/k_B T}, \quad (2)$$

80

81 where the index i numerates the stationary states of the cluster, H_{ni} is the energy of the i th state of the cluster, and f_n is the cluster Helmholtz free energy. According to Frenkel's model,¹ the cluster energy H_{ni} can be presented as the sum of translational, rotational, vibrational energies and the potential energy of the molecule interaction. All the clusters have one and the same structure corresponding to the minimum potential energy U_n . Thus, the cluster partition function may be written in the following form:

$$q_n = Q_{tr} Q_{rot} Q_{3n-6, \mathbf{v}} e^{-U_n/k_B T} \quad (3)$$

91 where Q_{tr} and Q_{rot} are the translational and the rotational partition functions, respectively, $Q_{3n-6, \mathbf{v}}$ is the partition function for $3n-6$ vibrational degrees of freedom (six degrees of freedom are deactivated because three translational and three rotational degrees of freedom are energized).

96 Equation (3) is written on the assumption that the cluster is solid. The last statement needs clarification. According to Frenkel,¹ the properties of liquid are akin to these of gases at high temperatures (near the critical point) and high specific volumes and rather similar to the properties of solids at low temperature and low specific volumes. The character of the thermal motion at low temperature in the liquid state (at least near the melting point) is about the same as in the solid state (i.e., small amplitude vibrations of molecules about the equilibrium positions). The last statement follows from the fact that the short-range order in the liquid state is about the same as in the solid one as well as from the low value of the melting enthalpy and small change in the specific volume and the heat capacity during the melting.

110 Following Debye's method in the theory of heat capacity of solids based on an approximate model of elastic, isotropic (i.e., amorphous) solids, Frenkel proposed a theory of the heat capacity of simple liquids for the temperatures near the melting point. He assumed that there was no qualitative difference between these liquids and the amorphous solids (overcooled liquid). According to Frenkel, the quantitative difference between ordinary liquids and amorphous solids is in a relatively short Maxwell relaxation time for liquids as compared to that for solids. The Maxwell relaxation time $\tau_M = \eta/G$, is the time which is necessary for the relaxation of the elastic shear stress (η is the coefficient of dynamic viscosity, G is the shear modulus).

123 For the ordinary temperature range Frenkel's estimations¹ have shown that the Maxwell relaxation time τ_M is approximately equal to the time τ of residence of particles in the temporary equilibrium positions (about which the harmonic oscillations occur):

$$\tau = \tau_0 \exp\left(\frac{W_0}{k_B T}\right), \quad (4)$$

128

129 where τ_0 is the period of harmonic oscillations, and W_0 is the free energy barrier for a molecule to overcome when jumping from one local minimum of potential energy to another. The activation energy can be evaluated approximately as¹

$$W_0 \cong 5k_B T_m, \quad (5) \quad 133$$

where T_m is the melting temperature. For the temperatures near the melting point the combination of Eqs. (4) and (5) gives

$$\tau_M \approx \tau \approx 100\tau_0. \quad (6) \quad 137$$

It follows from the Debye theory that the thermal motion of the system of elastically bound particles can be considered as a superposition of longitudinal and transverse waves with the wavelength to be in the range from the size of the body ($\lambda_{\max} \approx L$) to the distance $2r$ between the particles ($\lambda_{\min} \approx 2r$) (Ref. 1) (r is the radius of particles). Thus, the vibrational spectrum is limited between the Debye frequency⁹ (ν_{\max}),

$$\nu_{\max} \approx \frac{u}{\lambda_{\min}} \approx \frac{u}{2r}, \quad (7) \quad 146$$

and the minimum frequency,¹

$$\nu_{\min} \approx \frac{u}{\lambda_{\max}} \approx \frac{u}{L}, \quad (8) \quad 148$$

where u is the sound velocity.

Frenkel's theory accounts the contribution to the vibrational partition function from the whole spectrum of longitudinal waves. As to the transverse waves, this theory is able to account the contribution only from the high frequencies which satisfy the inequality,

$$\nu\tau_M \gg 1. \quad (9) \quad 155$$

The problem is that the transverse waves with frequencies less than $1/\tau_M$ are not able to propagate due to quick damping. The low frequency transversal vibrations are to be substituted by the motion of another kind. However, in the case of equilibrium cluster size distribution, small drops with the size L less than $10r$ dominate. Hence, the inequality Eq. (9) is correct for the whole spectrum of frequencies. Indeed, from Eqs. (7) and (8) for the drops with the size $L \approx 10r$ we have $\nu_{\min} \approx \nu_{\max}/5$. Then, taking into account that the Debye frequency¹ $\nu_{\max} \approx \tau_0^{-1}$, one gets from Eq. (6)

$$\nu\tau_M > \nu_{\min} \tau_M \approx \nu_{\max} \tau_M/5 \approx 20 \gg 1. \quad (10) \quad 166$$

The validity of the inequality Eq. (9) for the whole vibrational spectrum of a small cluster means that the cluster can be regarded as an amorphous solid. In this case Debye's theory can be applied to calculate the "internal" (vibrational) partition function and, hence, we can use formula (3) to calculate the full cluster partition function.

For the ordinary temperatures the vibrational partition function can be written as

$$Q_{3n-6, \mathbf{v}} = \prod_{\beta=1}^{3n-6} \frac{k_B T}{h \nu_{\beta}} = \left(\frac{k_B T}{h \nu_m}\right)^{3n-6} = (Q_{\mathbf{v}})^{3n-6}, \quad (11) \quad 175$$

where the product is made for all the $3n-6$ frequencies ν_{β} of normal vibrations of the cluster, ($\nu_{\min} < \nu_{\beta} < \nu_{\max}$), which are numerated by the index β , ν_m is the mean geometric frequency $\ln \nu_m = 1/3n-6 \sum_{\beta=1}^{3n-6} \ln \nu_{\beta}$, and $Q_{\mathbf{v}}$ is the partition

180 function for the oscillator with the frequency ν_m . Using
181 Eq. (11) one can rewrite Eq. (3) as

$$182 \quad q_n = \frac{Q_{\text{tr}} Q_{\text{rot}}}{(Q_{\text{v}})^6} Q_{3n, \text{v}} e^{-U_n/k_B T}, \quad (12)$$

183 or

$$184 \quad q_n = \frac{Q_{\text{tr}} Q_{\text{rot}}}{(Q_{\text{v}})^6} q_n^{\text{rest}}, \quad (13)$$

185 where q_n^{rest} is the partition function for the cluster at rest,

$$186 \quad q_n^{\text{rest}} = Q_{3n, \text{v}} e^{-U_n/k_B T} = e^{-f_n^{\text{rest}}/k_B T}, \quad (14)$$

187 f_n^{rest} is the Helmholtz free energy for the cluster at rest. Ac-
188 cording to the simple Frenkel model the free energy f_n^{rest} is
189 assumed to be given by¹

$$190 \quad f_n^{\text{rest}} = f_0 n + \gamma n^{2/3}, \quad (15)$$

191 where f_0 is the Helmholtz free energy per one molecule in
192 the bulk liquid phase, and γ is a constant proportional to the
193 surface tension of the flat interface. We refer to the factor
194 $Q_{\text{tr}} Q_{\text{rot}} / (Q_{\text{v}})^6$ in Eq. (13) as the Frenkel factor. Equation (15)
195 is the basis of the classical nucleation theory (CNT). In the
196 framework of CNT the embryo of the nucleating phase is
197 regarded as a spherical incompressible liquid drop fixed in
198 the space; the density of the drop is considered as homoge-
199 neous and equal to that of the bulk liquid. This drop has a
200 sharply defined interface with the surrounding metastable
201 mother phase which, in the case of vapor, is regarded as an
202 ideal gas; the surface tension of the critical nucleus is re-
203 garded as equal to that for the flat interface (“capillarity ap-
204 proximation”).

205 Using instead of Eq. (15) a similar formula for the Gibbs
206 free energy,

$$207 \quad g_n = \mu_l n + \gamma n^{2/3}, \quad (16)$$

208 where μ_l is the chemical potential of a molecule, as if it was
209 part of a bulk liquid at the pressure P outside of the drop,
210 Frenkel derived a formula for the cluster (drop) equilibrium
211 size distribution. This distribution proves to be¹

$$212 \quad N_n = N_1 \exp \left\{ -\frac{1}{k_B T} (g_n - \mu_{\text{v}} n) \right\}. \quad (17)$$

213 The rate of nucleation is proportional to the number N_{n^*} of
214 the critical nuclei^{1,8,10} (where n^* is the number of molecules
215 in the critical nucleus). Under the CNT approximation the
216 factor $(g_n - n\mu_{\text{v}})$ for the critical nucleus is equal to one-third
217 of the surface free energy.¹ Note, in the rigorous Gibbs
218 theory of interface,¹¹ one-third of the surface free energy is
219 equal to the work W of formation of the critical nucleus.
220 Thus, CNT is in a formal conformity with the rigorous Gibbs
221 theory.

222 Frenkel failed to find the connection between the size
223 distributions Eqs. (1) and (17). To do this, Lothe and Pound
224 considered an imaginary process (devised by Gibbs), in
225 which a cluster embedded in the bulk liquid is transferred to
226 the vapor phase.

In the Gibbs theory of interface W is governed by¹¹ 227

$$W = -V_S(P_l - P) + \sigma_s A_S, \quad (18) \quad 228$$

where P_l is the pressure of the reference bulk liquid having 229
the same temperature and chemical potential as the vapor, A_S 230
is the area of the surface of tension, which is assumed to be 231
spherical, V_S is the volume enclosed by this surface, and σ_s is 232
the surface tension. To make the meaning of Eq. (18) clearer, 233
Gibbs introduced an imaginary process consisting of two 234
separate stages. Let us consider this process in a nutshell. 235
Initially the system consists of the bulk liquid reference 236
phase (at pressure P_l) and the bulk vapor phase (at pressure 237
 P). Due to the pressure difference the reference phase is 238
surrounded by an elastic envelope. However, it is assumed 239
that the envelope is transmittable for the gas molecules. First, 240
some numbers of molecules from the vapor are transferred to 241
the bulk liquid. The volume of the reference phase increases 242
by V_S due to this transfer but the surface area is kept con- 243
stant. During this stage the benefit of work is $(P_l - P)V_S$. In 244
the next stage an aperture in the envelope opens and then 245
closes so that a volume V_S of the liquid phase is extruded 246
outside and the envelope intrudes inside to decrease the vol- 247
ume by the same magnitude V_S . The total work made at the 248
second stage is $\sigma_s A_S$. This work includes different compo- 249
nents. For instance, during the extrusion the drop loses the 250
interaction with the bulk liquid; therefore, $\sigma_s A_S$ contains the 251
energy of this interaction. $\sigma_s A_S$ includes also the work of 252
structural relaxation of the extruded drop and the adsorption 253
of gas molecules to its surface. 254

In the Gibbs thought process no account is taken of the 255
translational and rotational degrees of freedom of the cluster, 256
either in the bulk liquid or in the vapor. Lothe and Pound⁴ 257
suggested accounting the difference in free energy associated 258
with these degrees of freedom. They added to W the transla- 259
tional and rotational free energies of the cluster in the gas 260
phase and subtracted the entropy contribution to free energy 261
associated with the vibrational translation and rotation of the 262
embedded cluster with the relative positions of the molecules 263
in the cluster held fixed. The partition function correspond- 264
ing to those vibrational modes of fluctuation, q_{rep} , is called 265
the replacement partition function, since these modes are re- 266
placed by the free translation and free rotation in the vapor 267
phase. The above procedure results in the Lothe–Pound 268
factor,⁸ 269

$$\Phi_{\text{LP}} = \frac{Q_{\text{tr}} Q_{\text{rot}}}{q_{\text{rep}}} = \frac{Q_{\text{tr}}' Q_{\text{rot}}'}{Q_{\text{tr}}' Q_{\text{rot}}'}, \quad (19) \quad 270$$

where 271

$$q_{\text{rep}} = Q_{\text{tr}}' Q_{\text{rot}}', \quad (20) \quad 272$$

Q_{tr}' is the partition function of vibrational translations of the 273
embedded cluster, and Q_{rot}' is the partition function of vibra- 274
tional rotations around the center of mass of the cluster. 275

The factor Φ_{LP} is to substitute the Frenkel factor in Eq. 276
(13). As to the nucleation rate, it is to be multiplied to the 277
free energy correction factor Φ_{LP}/N_1 (the appearance of the 278
denominator N_1 will be discussed later). One should note that 279
it is assumed in the Lothe and Pound theory that Eq. (20) 280
refers to the absolutely incompressible cluster because the 281

relative coordinates of the n molecules in the cluster are fixed. Strictly speaking this assumption is not valid and can be considered only as an approximation even in the case of solid cluster (because solids are also compressible).

Approximating q_{rep} by $\exp(s/k_B)$ (where $s \approx 5k_B$ is the entropy of a single molecule in the bulk liquid) Lothe and Pound estimated the magnitude of Φ_{LP}/N_1 to be 10^{17} for the water cluster containing about 100 molecules.⁴ A correction factor this large appeared excessively large to many because the real discrepancy between the experimental measurements of nucleation rate and the classical theory predictions was not so high. Thus, a serious controversy developed since the beginning of Lothe–Pound theory. Reiss and co-workers introduced the concept of the so-called stationary cluster.^{5,6,10} The partition function of the stationary cluster is given by

$$q_n^{\text{st}} = \frac{1}{\Lambda^{3n} n!} \int_{r^n \in V^{\text{st}}} dr^n e^{-U_n/k_B T}, \quad (21)$$

where n particles are all confined to some volume V^{st} , which in turn is held fixed in space, U_n is particle's interaction potential, and Λ is the thermal wavelength of a particle. It was assumed that the reversible work of formation of the stationary cluster is equal to W [Eq. (18)]. The partition functions q_n and q_n^{st} are linked by the factor Φ_R (which we refer to as the Reiss factor),

$$q_n = \Phi_R q_n^{\text{st}}. \quad (22)$$

When deriving the expression for the factor Φ_R , Reiss and co-workers deactivated the rotational motion inside the volume V^{st} and the translational motion resulting from the fluctuation of the position of the center of mass of the stationary cluster prior to activating the free rotation corresponding to Q_{rot} and the free translation corresponding to Q_{tr} . Since the rotational motion of the n particles inside the volume V^{st} is essentially free rotation, no explicit account needs to be taken for the rotational partition function.¹⁰ Therefore, the Reiss factor is the ratio between the partition function for the free translations in the volume V and that for the translations of the center of mass in the volume V^{st} and proves to be^{6,10}

$$\Phi_R = \frac{V}{(2\pi)^{3/2} \sigma^3}, \quad (23)$$

where σ is the standard deviation in any of the three Cartesian coordinates of the center of mass, and $(\sqrt{2\pi}\sigma)^3$ is the volume in which the center of mass of the drop fluctuates. The evaluation of σ in the framework of the model of rigid spheres gives^{6,10}

$$\sigma = \frac{0.2 \mathbf{v}_n^{1/3}}{n^{1/2}} = \frac{(0.2)^3 \mathbf{v}_l^{1/3}}{n^{1/6}}, \quad (24)$$

where \mathbf{v}_n is the drop volume. Under the capillarity approximation $\mathbf{v}_n = n\mathbf{v}_l$, where \mathbf{v}_l is the volume per one molecule in the bulk liquid phase. If one assumes that $V^{\text{st}} = \mathbf{v}_n$, Eqs. (23) and (24) lead to the quantity $\Phi_R/N_1 \approx 10^6$ for a water cluster of 100 molecules.¹⁰ This value is considerably less than the estimation of Lothe and Pound for the ratio of translational partition functions $Q_{\text{tr}}/N_1 Q_{\text{tr}}^l \approx 10^{10}$. The difference between the evaluation of Reiss and that of Lothe and Pound is due to

the fact that in deriving Eq. (23) the assumption of the incompressibility of the liquid was not used.

In a more recent publication Reiss *et al.*¹² developed another approach where the isothermal compressibility coefficient appears explicitly so that the new expression for the Reiss factor is

$$\Phi_R' = \frac{V}{\sigma_n}, \quad (25)$$

where σ_n is the variance of the volume fluctuation in the standard formulation of the constant pressure ensemble,

$$\sigma_n = (k_B T \kappa \mathbf{v}_n)^{1/2} \approx n^{1/2} (k_B T \kappa \mathbf{v}_l)^{1/2}. \quad (26)$$

The resulting value of Φ_R'/N_1 is about 10^4 divided by the supersaturated ratio for a water cluster consisting of 100 molecules. Note that Φ_R'/N_1 is about 100 times less than Φ_R/N_1 which is due to the fact that the variance of volume fluctuation σ_n is about 100 times larger than the volume $(\sqrt{2\pi}\sigma)^3$ in which the center of mass of the drop fluctuates.¹⁰ Note, as seen from the comparison between Eqs. (24) and (26), this difference must increase with increasing drop size because σ_n increases and σ^3 decreases with increasing n . Reiss notes reasonably¹⁰ that in the theory of Lothe and Pound the translational degrees of freedom are to be related to the motion of the center of mass of the embedded (compressible) cluster with respect to the fixed spherical boundary of the cluster but not to the vibrational translation of the rigid cluster as a whole.

On the other hand, Reiss believes that in the theory of Lothe and Pound (as well as in the case of stationary cluster) the ratio $Q_{\text{rot}}/Q_{\text{rot}}^l$ is about unity assuming that the rotation of a drop which is a part of a bulk liquid is essentially the same as the free rotation,¹⁰ i.e., no explicit account needs to be taken for the rotational partition function (as well as in the case of stationary cluster). Besides, he stated¹⁰ that the free energy of the interaction between the embedded drop and the ambient bulk liquid was already included into the surface free energy $\sigma_S A_S$. One can agree with the statement that $Q_{\text{rot}}/Q_{\text{rot}}^l$ is about unity only in the case of high temperatures. But at the temperature near the melting point (typical temperatures for homogeneous nucleation experiments) the mechanical behavior of the viscous liquid is to be more similar to that of the solid in the case of quick processes (for the time shorter than the Maxwell relaxation time).¹ The second statement of Reiss about the free energy of interaction to be included to the surface free energy is also disputable. The only evident fact is that the potential energy of the interaction between the drop and the outer molecules must be included into the surface free energy in any case. However, there is also an entropy contribution to the free energy related to the hindrance of the rotational and translational movements of the embedded cluster due to its interaction with the surrounding liquid. The last contribution will be lost after the cluster extrusion to the gas. At the same time the embedded drop is at rest in the Gibbs imaginary process and, therefore, no contribution to $\sigma_S A_S$ due to the loss of the rotational movement should be implicated. Therefore Nishioka and Pound^{13–15} included the entropy of rotational movement of the embedded cluster to q_{rep} but not to $\sigma_S A_S$ as in contrast

389 to Reiss. We shall not discuss this complicated question thor-
390 oughly and take the side of Nishioka and Pound.

391 III. THEORY OF KUSAKA AND APPROXIMATE 392 ANALYTICAL FORMULA FOR THE CORRECTION 393 FACTOR

394 As is seen from the above-said, the theory of Lothe and
395 Pound considers the thought Gibbs extrusion process but
396 uses rather rough and ill-founded approximations. Therefore
397 it seems to be clear that the approximate formula of Lothe
398 and Pound [Eq. (19)] cannot be used as a basis for the cal-
399 culation of correction factor. To derive a formula suitable for
400 such a calculation, Kusaka developed a rigorous statistical-
401 mechanical approach⁸ based on the Gibbs extrusion process
402 considered in Sec. II. Let us look at the milestones of
403 Kusaka's theory.

404 The isothermal-isobaric partition function of the bulk
405 liquid held at constant (T, P_l, N) is⁸

$$Y(T, P_l, N) = \int \frac{dV}{a} \frac{\exp\left(-\frac{P_l V}{k_B T}\right)}{h^{3N} N!} \int d\mathbf{p}^N d\mathbf{r}^N \exp\left(-\frac{H_N}{k_B T}\right), \quad (27)$$

406 where p^N collectively denotes the momentum of each of the
407 N particles, and H_N is the system Hamiltonian. The constant
408 a arises from the mechanical degrees of freedom of a piston
409 imposing the constant pressure P_l . Then a cluster embedded
410 in the bulk liquid phase is defined by taking a spherical re-
411 gion of volume V_S , which contains m particles. The phase
412 points embraced by Eq. (27) are partitioned according to the
413 number m of molecules inside the spherical region:

$$Y(T, P_l, N) = \int \frac{dV}{a} \exp\left(-\frac{P_l V}{k_B T}\right) \sum_{m=3}^N \frac{1}{h^{3(N-m)} (N-m)!} \int_{r^{N-m} \in V-V_S} d\mathbf{p}^{N-m} d\mathbf{r}^{N-m} \\ \times \exp\left(-\frac{H_{N-m}}{k_B T}\right) \frac{1}{h^{3m} m!} \int_{r^m \in V_S} d\mathbf{p}^m d\mathbf{r}^m \\ \times \exp\left(-\frac{H_m}{k_B T}\right) \exp\left(-\frac{U_{\text{int}}}{k_B T}\right), \quad (28)$$

419 where U_{int} denotes the interaction potential between the N
420 $-m$ particles outside the sphere and the m particles inside the
421 sphere, and is a function of r^{N-m} and r^m . The last integral in
422 Eq. (28), along with the coefficient $1/h^{3m} m!$, is regarded as
423 the partition function ξ_m of a cluster, which consists of m
424 particles, all confined to V_S , and is embedded in the liquid
425 phase.

426 The coordinate transformation is to be done from a labo-
427 ratory system to a body coordinate system which means that
428 a set of Euler axes is embedded in the object with the origin
429 at the center of mass $\mathbf{R}_{\text{c.m.}}$ and the rotation refers to the
430 rotation of these axes. Denoting by s^{m-2} and t^{m-2} the coordi-

nates and the conjugate momenta of the remaining $3m$
-6 degrees of freedom of the embedded cluster, the partition
function ξ_m is written as⁸

$$\xi_m = \frac{1}{h^{3m-6} m!} \int_{r^m \in V_S} dt^{m-2} ds^{m-2} \exp\left(-\frac{K_S}{k_B T}\right) \\ \times \exp\left(-\frac{U_m}{k_B T}\right) \frac{s_1 s_2 s_3}{\Lambda_{\text{c.m.}}^3} \int_{r^m \in V_S} d\mathbf{R}_{\text{c.m.}} \sin \theta d\theta d\phi d\psi \\ \times \exp\left(-\frac{U_{\text{int}}}{k_B T}\right), \quad (29)$$

where K_S is the kinetic energy of the m particles excluding
those due to rigid translation and rotation of the embedded
cluster as a whole, U_m is the interaction potential among the
 m particles, and the Euler angles (θ, ϕ, ψ) specify the orien-
tation of the cluster; $\Lambda_{\text{c.m.}}$ and s_i are $\Lambda_{\text{c.m.}} = h / \sqrt{2\pi M k_B T}$ and
 $s_i = \sqrt{2\pi I_i k_B T} / h$ with M and $I_i (i=1, 2, 3)$ denoting the mass
of the cluster and its principal moments of inertia, respec-
tively.

The second integral in Eq. (29) is regarded as the con-
figurational partition function Z_c of the embedded cluster due
to its translational and rotational degrees of freedom when it
is subjected to the external field U_{int} . Thus, the configura-
tional entropy S_c associated with these degrees of freedom is
defined by means of the equation

$$Z_c = \int_{r^m \in V_S} d\mathbf{R}_{\text{c.m.}} \sin \theta d\theta d\phi d\psi \exp\left(-\frac{U_{\text{int}}}{k_B T}\right) \\ = \delta^3 \exp\left(-\frac{\langle U_{\text{int}} \rangle_c}{k_B T}\right) \exp\left(\frac{S_c}{k_B T}\right), \quad (30)$$

where $\langle \cdots \rangle_c$ denotes the thermal average taken with the Bolt-
zmann weight $\exp(-U_{\text{int}}/k_B T)$ while imposing the con-
straint $r^m \in V_S$ that the m particles are confined to the volume
 V_S .

The quantity δ is an arbitrary length scale in Eq. (30) and
is introduced to make explicit the dimensionality of various
quantities involved. Kusaka believes that a natural choice for
 δ is to identify it with some characteristic length scale of the
system and he identifies it with the particle diameter. He
notes that the numerical value of Z_c , and hence that of
 $\delta^3 \exp(S_c/k_B T)$, depends only on the functional form of
 $U_{\text{int}}/k_B T$ and the unit used to measure a length. Once they are
specified, the numerical value of $\delta^3 \exp(S_c/k_B T)$ is stated to
be independent of the choice of δ . The last statement is true,
but one must understand that the numerical value of S_c does
depend on the choice of δ . Therefore, the entropy S_c thus
defined is some "formal entropy." Later we will discuss this
question in more detail.

Since the coordinates r^{N-m} and s^{m-2} are fixed when
evaluating Z_c one can say that the cluster which is governed
by Eq. (30) is a rigid one in a rigid environment. The idea of
Kusaka is that during the extrusion of such a cluster the
modes of fluctuation associated with the factor,

$$\frac{s_1 s_2 s_3}{\Lambda_{c.m.}^3} \delta^3 \exp\left(\frac{S_c}{k_B}\right), \quad (31)$$

are to be deactivated. Then, the resulting equation for q_{rep} is⁸

$$\frac{1}{q_{\text{rep}}} = \left\langle \left(\frac{s_1 s_2 s_3}{\Lambda_{c.m.}^3} \delta^3 \exp\left(\frac{S_c}{k_B}\right) \right)^{-1} \right\rangle_l, \quad (32)$$

where $\langle \dots \rangle_l$ indicates a thermal average taken in the bulk liquid held at constant (T, P_l, N) .

On the other hand, according to Kusaka, the activation of the free translation within the volume V and the free rotation of the extruded cluster, when averaged over all possible values of m and internal configurations s^{m-2} , leads to the factor

$$Q_{\text{tr}} Q_{\text{rot}} = \left\langle \frac{s_1 s_2 s_3}{\Lambda_{c.m.}^3} \right\rangle_l 8\pi^2 V. \quad (33)$$

Upon the extrusion, the m -sized cluster loses its interaction U_{int} with the surroundings, acquires $n-m$ particles from the vapor phase, and then undergoes the structural relaxation. Thus, the translational and the rotational partition functions of the n -sized cluster differ from the corresponding quantities given in Eq. (33) for the m -sized cluster. Nevertheless, as in the original Lothe–Pound prescription, Kusaka assumes that the reversible work associated with these processes is included fully in σ_S . Uniting Eqs. (32) and (33) Kusaka arrives finally at the expression for factor Φ_K (which we refer to as the Kusaka factor) designated to substitute the Lothe–Pound factor,

$$\Phi_K = \left\langle \frac{s_1 s_2 s_3}{\Lambda_{c.m.}^3} \right\rangle_l 8\pi^2 V \left\langle \left(\frac{s_1 s_2 s_3}{\Lambda_{c.m.}^3} \delta^3 \exp\left(\frac{S_c}{k_B}\right) \right)^{-1} \right\rangle_l. \quad (34)$$

Our task now is to obtain an analytical formula applicable for a semiquantitative evaluation of the Kusaka factor. To solve this task, we will analyze the key equation of the theory of Kusaka [Eq. (30)]. Actually for all the m -sized clusters which happened to be inside the volume V_S the cluster's volume $\mathbf{v}_m < V_S$. Thus, there is some volume $V_S - \mathbf{v}_m$ accessible for the rigid cluster motion. Hence, there is some volume $\Delta V_{c.m.}$ accessible for the motion of the cluster's center of mass. Note, $\Delta V_{c.m.}$ is the volume over which the integration is made in Eq. (30). It is clear that the larger the difference $V_S - \mathbf{v}_m$, the larger the volume $\Delta V_{c.m.}$, and, consequently, the larger is Z_c [and, hence, $\delta^3 \exp(S_c/k_B)$]. Assuming that the average volume $\langle V_S - \mathbf{v}_m \rangle$ is approximately equal to the variance of the volume fluctuation σ_m we may state that the larger the σ_m , the larger the $\delta^3 \exp(S_c/k_B)$ (and the smaller the Φ_K). Note, the last conclusion is in a qualitative agreement with Eq. (25) for the Reiss factor Φ'_R .

On the other hand, the average magnitude of the volume $\Delta V_{c.m.}$ over which the integration is made in Eq. (30) is not equal to σ_m but essentially less. It is useful to evaluate $\langle \Delta V_{c.m.} \rangle$. To this end we assume that $\langle V_S - \mathbf{v}_m \rangle \cong \sigma_m$ and $V_S \cong \mathbf{v}_m = m\mathbf{v}_l$. We assume also that the volume $\Delta V_{c.m.}$ over which the center of mass $\mathbf{R}_{c.m.}$ is sweeping in the integration is spherical. Let $\langle d \rangle$ be the diameter of the average integration volume $\langle \Delta V_{c.m.} \rangle$. As the cluster is rigid (the coordinates s^{m-2} are fixed) the radius of this volume $\langle d \rangle/2$ is equal to the

width of the spherical layer between the equicentered volumes V_S and \mathbf{v}_m . Assuming that this width is small we have

$$\frac{\langle d \rangle}{2} \cong \frac{\langle V_S - \mathbf{v}_m \rangle}{4\pi R_S^2} \cong \frac{\sigma_m}{4\pi R_S^2}, \quad (35)$$

where R_S is the radius of the spherical volume V_S . Then, accounting the above simplifications and Eq. (26), one gets

$$\langle \Delta V_{c.m.} \rangle = \frac{\pi \langle d \rangle^3}{6} = \frac{k_B T \kappa}{27 \mathbf{v}_m} \sigma_m = \frac{k_B T \kappa}{27 \mathbf{v}_m} \sigma_m. \quad (36)$$

For the representative case of water cluster for $T=300$ K, ($\kappa=5 \times 10^{-11}$ cm²/dyne and $\mathbf{v}_l=3 \times 10^{-23}$ cm³) we have $\sigma_m \approx 8 \times 10^{-24} \sqrt{m}$ cm³, $\langle \Delta V_{c.m.} \rangle = 10^{-2}/4m \sigma_m \cong 2 \times 10^{-26}/\sqrt{m}$ cm³ and $\langle d \rangle \approx \langle \Delta V_{c.m.} \rangle^{1/3} \approx 2.7 \times 10^{-9}/m^{1/6}$ cm. The above evaluations have shown that the variance of the volume fluctuation σ_m for the cluster of size $m=100$ is about the molecular volume v_l ; the average volume accessible for the motion of the center of mass $\langle \Delta V_{c.m.} \rangle$ is much less than σ_m and equal to $\langle \Delta V_{c.m.} \rangle \approx 10^{-4} \mathbf{v}_l$. As a consequence, the diameter $\langle d \rangle$ of the average integration volume is by an order of magnitude less than molecule diameter.

The above estimations are rather rough but show that the size of the integration region is small enough, i.e., the variation of $\mathbf{R}_{c.m.}$ when taking the integral in Eq. (30) occurs in a very narrow region. Therefore, the variation of the integrand function U_{int} is rather weak during the integration over $d\mathbf{R}_{c.m.}$. Thus, we can consider the interaction potential U_{int} as independent of $\mathbf{R}_{c.m.}$. Then the integral in Eq. (30) can be written as the product of two integrals and we arrive at

$$Z_c = d^3 \int_{r^m \in V_S} \exp\left(-\frac{U_{\text{int}}}{k_B T}\right) \sin \theta d\theta d\phi d\psi \\ = d^3 \exp\left(\frac{S'_c}{k_B}\right) \exp\left(-\frac{\langle U_{\text{int}} \rangle_c}{k_B T}\right), \quad (37)$$

where $d^3 = \Delta V_{c.m.}$.

The integral in Eq. (37) may be regarded as the configurational partition function of the embedded cluster due to its rotational degrees of freedom only, when it is subjected to the external field $U_{\text{int}}(\theta, \phi, \psi)$. As a consequence, the configurational entropy S'_c is associated here with these degrees of freedom, i.e., it has a definite physical sense of the entropy linked with the cluster's rotational motion [as in contrast with the effective entropy in Eq. (30)]. The entropy S'_c has a definite physical sense now, because instead of the arbitrary length scale δ in Eq. (30) we have in Eq. (37) a definite and natural characteristic length scale of the system d which is the size of the integration area. This quantity d substitutes now δ in Eq. (34). We assume now that the average values in Eq. (34) can be substituted by the products of averages:

$$\Phi_K \approx \frac{\langle s_1 s_2 s_3 \rangle_l}{\langle \Lambda_{c.m.}^3 \rangle_l} 8\pi^2 V \frac{\langle \Lambda_{c.m.}^3 \rangle_l}{\langle d^3 \rangle_l \left\langle s_1 s_2 s_3 \exp\left(\frac{S'_c}{k_B}\right) \right\rangle_l}. \quad (38)$$

One more assumption is made that the average magnitude of the volume d^3 over which the center of mass sweeps

571 during the integration in Eq. (30) is approximately equal to
 572 the volume in which the center of mass of the drop of vol-
 573 ume V_S fluctuates:

$$574 \quad \langle d^3 \rangle_l = (\sqrt{2\pi}\sigma)^3. \quad (39)$$

575 In Eq. (39) σ must be expressed by [see Eq. (24)]:

$$576 \quad \sigma = \frac{(0.2)V_S^{1/3}}{\langle m \rangle_l^{1/2}} = \frac{(0.2)V_S^{1/3}}{(\rho_l V_S)^{1/2}} = \frac{(0.2)}{\rho_l^{1/2} V_S^{1/6}}, \quad (40)$$

577 where $\langle m \rangle_l = \rho_l V_S$ and ρ_l is the particle number density of the
 578 reference bulk liquid.

579 After the cancellation and using Eq. (39) we get from
 580 Eq. (38):

$$581 \quad \Phi_K \equiv \Phi_R \frac{Q_{\text{rot}}^K}{Q_{\text{rot},l}^K}, \quad (41)$$

582 where Φ_R is the Reiss factor [Eq. (23)] in which σ is de-
 583 scribed by Eq. (40). The quantity Q_{rot}^K in the denominator of
 584 Eq. (41) is $Q_{\text{rot}}^K = 8\pi^2 \langle s_1 s_2 s_3 \rangle_l$, where $\langle \dots \rangle_l$ denotes the ther-
 585 mal averaging for various values of m taken with respect to
 586 the isothermal-isobaric ensemble representing the bulk liq-
 587 uid. Due to this averaging Q_{rot}^K has a physical sense of the
 588 rotational partition function for a free drop in the vapor, but
 589 not for a cluster. According to Kusaka⁸ this drop contains
 590 $\langle m \rangle_l = \rho_l V_S$ particles and is a ball of radius R_S with the homo-
 591 geneous density ρ_l . Therefore, we must write

$$592 \quad Q_{\text{rot}}^K = \frac{\sqrt{\pi}(8\pi^2 I k_B T)^{3/2}}{h^3}, \quad (42)$$

593 where I is the moment of inertia of the spherical drop,

$$594 \quad I = \frac{8}{15} \pi R_S^5 \rho, \quad (43)$$

595 $\rho = \rho_l \mu$ is the density of the reference bulk liquid (here μ is
 596 the molecule mass).

597 Finally, the quantity $Q_{\text{rot},l}^K$ is

$$598 \quad Q_{\text{rot},l}^K = \left\langle s_1 s_2 s_3 \exp\left(\frac{S'_c}{k_B}\right) \right\rangle_l. \quad (44)$$

599 As was shown above the quantity S'_c in Eq. (38) [as well as
 600 in Eq. (44)] has a physical sense of the entropy related to the
 601 rotational movement of embedded cluster. Therefore, $Q_{\text{rot},l}^K$
 602 [due to the averaging in Eq. (44)] has a sense of the rota-
 603 tional partition function for the embedded spherical drop of
 604 volume V_S . Following Frenkel's views one can hope that the
 605 rotational movement of such a drop with respect to the en-
 606 vironmental viscous liquid at low enough temperature near
 607 the melting point will be like the rotational vibrations of a
 608 solid body. The necessary condition for this kind of vibra-
 609 tions is that the period of vibrations T_v be small with regards
 610 to the Maxwell relaxation time τ_M of shear stress which oc-
 611 curs during the drop rotations¹ $T_v \ll \tau_M$ or $\nu \tau_M \gg 1$ (where
 612 $\nu = 1/T_v$ is the vibrational frequency). The last inequality is
 613 exactly the inequality Eq. (9) and, as seen above in Sec. II,
 614 one can hope that this inequality is valid for the vibrational
 615 processes with the frequency ν equal to the Debye frequency
 616 (or even less).

There is a series of publications devoted to the evalua- 617
 tion of the vibrational frequency of the solid cluster.¹⁶⁻¹⁸ 618
 These evaluations have shown that the frequency of rota- 619
 tional vibrations ν of small clusters with the number of mol- 620
 ecules $n \approx 100$ is about the Debye frequency ν_{max} . Account- 621
 ing that at the ordinary temperatures the partition function of 622
 oscillator depends weakly enough (only linearly) on fre- 623
 quency one can use the simplest formula for the vibrational 624
 frequency¹⁶ $\nu \approx \sqrt{3} n^{-1/6} \nu_{\text{max}}$. One can see that this formula 625
 gives $\nu \approx \nu_{\text{max}}$ for $n=27$. We suppose that the equation ν 626
 $\approx \nu_{\text{max}}$ is valid for all the small clusters. Thus, we assume 627
 that the rotational partition function $Q_{\text{rot},l}^K$ can be written as 628
 the vibrational partition function for three degrees of free- 629
 dom: 630

$$Q_{\text{rot},l}^K \equiv (Q_v)^3 \equiv \left\{ \exp\left(\frac{h\nu_{\text{max}}}{2k_B T}\right) \left[1 - \exp\left(-\frac{h\nu_{\text{max}}}{k_B T}\right) \right] \right\}^{-3}. \quad (45) \quad 631$$

IV. AN ASSEMBLY OF DROPS: THE CORRECTION 632 FACTOR FOR THE NUCLEATION RATE 633

The Kusaka factor considered in the previous section is 634
 to give a connection between the partition function (q_n^{rest}) of 635
 the drop at rest and the partition function (q_n) of the drop at 636
 motion: 637

$$q_n = \Phi_K q_n^{\text{rest}} = \Phi_K \exp\left(-\frac{f_n^{\text{rest}}}{k_B T}\right). \quad (46) \quad 638$$

Note, the drop at rest is implied here to be such a drop the 639
 work of formation for which W is governed by the expres- 640
 sion Eq. (18) derived by Gibbs; f_n^{rest} is the Helmholtz free 641
 energy for this drop. Strictly speaking, Eq. (18) is valid only 642
 for the critical nucleus, and an additional term arises when 643
 the Gibbs theory of interface is properly extended to treat 644
 nonequilibrium clusters.¹⁹⁻²³ However, the rate of nucleation 645
 is proportional to the number N_{n^*} of the critical nuclei.^{1,8,10} 646
 Therefore, to evaluate the nucleation rate, one should know 647
 just the work of formation of these critical nuclei. 648

To know the number of critical nuclei, one should derive 649
 the equilibrium drop size distribution. We will use the ap- 650
 proach of Reiss⁷ to obtain this distribution. To determine the 651
 equilibrium size distribution, Reiss considered an ensemble 652
 of physical clusters as an ideal gas mixture.¹⁰ It was sup- 653
 posed in this model that these clusters did not interact with 654
 the molecules of the environmental ideal vapor. Therefore, 655
 the full partition function for the system of volume V con- 656
 sisting of N_n drops and N_1 ideal vapor monomeric molecules 657
 can be written in the following form:⁷ 658

$$Q(V) = \sum_{\{N_n\}} Q_{N_1, N_n}^{\text{id}} \left(V - \sum_{n=2} N_n \mathbf{v}_n \right) \prod_{n=2} \frac{q_n^{N_n}}{N_n!}, \quad (47) \quad 659$$

where Q_{N_1, N_n}^{id} is the partition function of ideal vapor. The first 660
 sum in Eq. (47) is over all distributions N_n such that 661

$$N_1 + \sum_{n=2} nN_n = N, \quad (48)$$

where N is the total number of molecules in the system and the superscript *id* indicates “ideal.” The equilibrium distribution is found in the usual manner by finding the maximum term in the sum of Eq. (47) subject to the conservation condition, Eq. (48). The result is⁷

$$N_n = q_n \exp\left\{-\frac{1}{k_B T}(P\mathbf{v}_n - n\mu_{\mathbf{v}})\right\}, \quad (49)$$

where P is the ambient ideal gas pressure. The substitution of Eq. (46) into Eq. (49) yields

$$N_n = \frac{\Phi_K}{N_1} N_1 \exp\left\{-\frac{f_n^{\text{rest}} + P\mathbf{v}_n - n\mu_{\mathbf{v}}}{k_B T}\right\}, \quad (50)$$

where $f_n^{\text{rest}} + P\mathbf{v}_n = g_n^{\text{rest}}$ is the Gibbs free energy for the drop at rest. Formula (50) differs from the CNT expression for the drop size distribution¹ [Eq. (17)] by the factor Φ_K/N_1 . Thus, the classical formula Eq. (17) is to be modified by the correction factor Φ_K/N_1 and, as the nucleation rate is proportional to the number N_{n^*} of critical nuclei, the same free energy correction factor will appear in the classical expression for the nucleation rate. One can see also that the coefficient $1/N_1$ appeared in the free energy correction factor naturally.

It is important to note that Eq. (17) for the drop size distribution was derived in CNT (Ref. 1) basing on the rough approximation expressed by Eq. (16). As to the Reiss approach, the only simplification made when deriving Eq. (50) for the drop size distribution was the ideal gas mixture approximation. The expression in the numerator of the exponent in the classic Eq. (17) is the Gibbs free energy change. It is merely claimed in CNT that for the critical drop this change is equal to the work of the drop formation. On the other hand, the expression in the numerator of the exponent in Eq. (50) is also the change of Gibbs free energy in the process of formation of n -sized drop at rest from n vapor molecules. However, in the last case the Gibbs free energy change in the process of the critical drop formation is really equal to the reversible work W of formation of this drop (in the framework of the ideal gas mixture approximation) (see Appendix).

V. COMPARISON WITH KUSAKA'S NUMERICAL SIMULATION RESULTS

Basing on Eqs. (23), (41)–(43), and (45) we propose the following approximate equation for the correction factor Φ/N_1 :

$$\begin{aligned} \frac{\Phi}{N_1} &= \frac{\Phi_R}{N_1} \frac{Q_{\text{rot}}^K}{Q_{\text{rot},l}^K} \\ &= \frac{\Phi_R}{N_1} \frac{Q_{\text{rot}}^K}{(Q_{\mathbf{v}})^3} = \frac{1}{S n_1^{\text{sat}} (2\pi)^{3/2} \sigma^3} \pi^5 \left(\frac{64R_S^5 \rho k_B T}{15h^2}\right)^{3/2} \\ &\quad \times \exp\left(\frac{3h\nu_{\text{max}}}{2k_B T}\right) \left\{1 - \exp\left(-\frac{h\nu_{\text{max}}}{k_B T}\right)\right\}^3, \end{aligned} \quad (51)$$

where S is the supersaturation ratio, n_1^{sat} is the saturated vapor number density, σ and n_{max} are to be evaluated via Eqs. (40) and (7), respectively.

Kusaka⁸ evaluated the correction factor for the Lennard-Jones fluid by the numerical simulation for the reduced temperature range 0.7–0.9 [the reduced temperature (T^*) is defined as $T^* = k_B T / \varepsilon$, where ε is the characteristic energy of the Lennard-Jones potential]. Here in this section we will compare the correction factor Φ/N_1 as estimated via Eq. (51) for Ar with that as determined by Kusaka (Φ_K/N_1). To compare Φ/N_1 with Φ_K/N_1 one needs to know the density ρ of the reference bulk liquid, the sound velocity u in the bulk liquid, the supersaturation ratio S , and n_1^{sat} . The density of the bulk liquid can be retrieved from Kusaka's computer simulation results⁸ as a function of temperature

$$\rho = 2.03 - 8.3 \times 10^{-3} T(\text{K}) \text{ (g/cm}^3\text{)}. \quad (52)$$

The supersaturation ratio can be obtained using the computer simulation data of ten Wolde and Frenkel²⁴ for the homogeneous gas-liquid nucleation in the Lennard-Jones system. To use these data one should bring into correspondence the radius of the surface of tension R_S (used by Kusaka⁸) with the equimolar radius R_e (which is a characteristic of the clusters studied by ten Wolde and Frenkel). These two radii are related by the equation $R_e = R_S + \delta$, where δ is the so-called Tolman length. The radius of the surface of tension was chosen $R_S = 1.8, 2.0, 2.5$ (in Lennard-Jones units) in Kusaka's numerical simulation.⁸ The Lennard-Jones parameters for Ar are $\sigma_{\text{LJ}} = 0.34$ nm and $\varepsilon/k_B = 119.8$ K. Thus, one gets $R_S = 0.61, 0.68, \text{ and } 0.85$ nm, respectively. The Tolman length was determined by Bartell²⁵ for Ar for the reduced temperature $T^* = 0.74$ as a function of R_S . For $R_S = 0.61, 0.68, \text{ and } 0.85$ nm the Tolman length reads²⁵ $\delta = 0.20, 0.18, \text{ and } 0.14$ nm, which gives $R_e = 0.81, 0.86, \text{ and } 0.99$ nm, respectively. Thus, for example, using Eq. (52) we have for $R_e = 0.86$ nm the number of molecules in the drop $m = 52$. The critical supersaturation for the clusters of that size is²⁴ $S \approx 2$. Therefore, we used this value of the supersaturation ratio in our estimations of the correction factor.

For $T^* = 0.74$ the pressure in the bulk reference phase (which has the same chemical potential as the gas at supersaturation $S = 2$) was taken from Ref. 24 as equal to 0.36 (in Lennard-Jones units) which is about 150 atm. for argon. The argon sound velocity for this pressure can be approximated by the equation^{26–28} $u = 1.46 \times 10^5 - 6.34 \times 10^2 T(\text{cm/s})$. Finally, ν_{max} was evaluated as $\nu_{\text{max}} = u/2r = u/\sigma_{\text{LJ}}$. To evaluate n_1^{sat} the expression for the saturated vapor pressure of argon was used,²⁹ $\log_{10}(P/\text{Torr}) = 7.76 - 420.62/T$.

Figure 1 shows the correction factor Φ/N_1 as calculated via Eq. (51) for $R_S = 2.0$ as well as the contributions to this factor from Φ_R/N_1 , Q_{rot}^K and $(Q_{\mathbf{v}})^{-3}$. What is important is that the contribution from the translational degrees of freedom Φ_R/N_1 is in the range $3 \times 10^2 - 10^4$, while the main contribution comes from the rotational degrees of freedom Q_{rot}^K which is about 3×10^7 in the temperature range 80–110 K. The vibrational contribution $(Q_{\mathbf{v}})^{-3}$ is small enough being in the range 1–8, which corresponds to the range of $Q_{\mathbf{v}}$ from 1 to 0.5. Such a small magnitude of the vibrational partition function corresponds to the condition $k_B T < h\nu_{\text{max}}$, i.e., to the

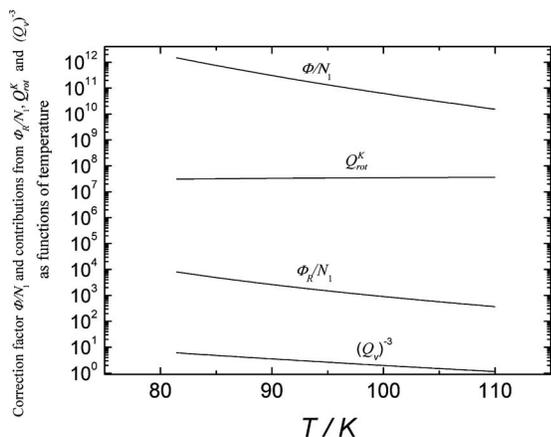


FIG. 1. Correction factor Φ/N_1 [Eq. (51)] and contributions from Φ_R/N_1 [Eqs. (23) and (40)], Q_{rot}^K [Eqs. (42) and (43)], and $(Q_v)^{-3}$ [Eq. (45) for $R_S=2.0$] (in Lennard-Jones units).

low-temperature limit where the quantum nature of the oscillator is to be accounted; that is why the Eq. (45) was written in the quantum form.

Figure 2 compares the correction factor Φ/N_1 and that of Kusaka Φ_K/N_1 for $R_S=1.8, 2.0,$ and 2.5 . One can see that these two factors are in a good agreement with each other. Φ/N_1 and Φ_K/N_1 coincide ideally for $R_S=2.5$; and for $R_S=2.0$ and 1.8 the agreement is within the factor of 2. The temperature dependence of Φ/N_1 is in an excellent agreement with that of Φ_K/N_1 . As one can see from Fig. 1 the dominant contribution to the temperature dependence comes from the Reiss factor Φ_R/N_1 (the temperature dependence of this factor is mainly governed by the concentration n_1^{sat}). However, the last factor $(Q_v)^{-3}$ in Eq. (51) also depends significantly on temperature. The temperature dependence for $(Q_v)^{-3}$ is mainly governed by the first factor in Eq. (45) which is to account the zero-point vibrations. Not accounting this factor one will lose the agreement between the temperature dependencies of Φ/N_1 and Φ_K/N_1 .

The excellent agreement between the temperature dependencies for Φ/N_1 and Φ_K/N_1 supports our assumption that the internal degrees of freedom which are to be deactivated are, actually, the torsion vibrations. One may also note that

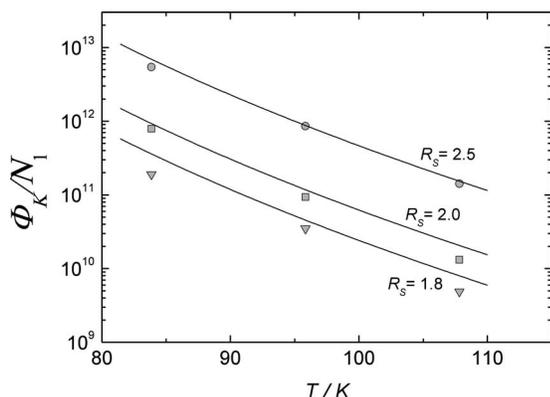


FIG. 2. Free energy correction factor for different values of the drop radius R_S vs temperature. Symbols: numerical calculations by Kusaka (Ref. 8). Lines: as evaluated via Eq. (51). The magnitudes of R_S are shown in Lennard-Jones units.

the agreement between the temperature dependencies for Φ/N_1 and Φ_K/N_1 means, in particular, that the enlargement of free volume in the liquid phase during the temperature increase is not so high to influence essentially the character of the rotational motion of the embedded cluster. One can state with high enough accuracy that after the temperature increase this motion is still vibrational but not a free rotation (which would give the partition function exaggerated by orders of magnitude). In this case one may expect that some change in pressure in the liquid at $T=\text{const}$ also would not give any noticeable change in the character of rotational motion. Note that the numerical simulation⁸ has shown that the Kusaka correction factor was really insensitive to the liquid pressure.

Formula (51) is considered as semiquantitative. Thus, for example, the choice of the torsion vibration frequency is rather approximate. Nevertheless this formula agrees with Kusaka's simulation results with a factor of 2 which is within the accuracy of simulation. Therefore it seems to be of no reason to try to find a more exact (and, consequently, more complicated) expression for the correction factor. We believe that the simple formula Eq. (51) will be useful for specialists in the field of nucleation from vapor to evaluate the nucleation rate and to have a reference when comparing different systems.

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APPENDIX:

In this section we will evaluate the exponent in Eq. (50) for the drops which are in an unstable equilibrium with the vapor. In order to make this evaluation it is useful to consider the Gibbs reversible process of formation of a spherical liquid drop at rest inside the bulk vapor phase.¹¹ In accordance with the nomenclature of Gibbs¹¹ we will refer, respectively, to $[\varepsilon]$, $[\eta]$, and $[N]$ as the excesses of energy, entropy, and number of molecules inside and around the drop with regard to those in the space without the drop (i.e., filled only with the vapor). We shall refer to ε'_v , η'_v , and γ' as the densities of energy, entropy, and number of molecules in the vapor phase, respectively. As the total system volume V and mass are very large, the densities of energy, entropy, and number of molecules can be considered as constant during the process. The gas pressure P' [nominated as P in Eq. (50)] is constant as well. However, strictly speaking, after the drop formation the pressure in the real gas will be equal to P' only far enough

842 from the drop. Near the drop the gas pressure will differ from
843 P' due to the interaction between the gas molecules and the
844 drop. By definition,

$$845 \quad [\varepsilon] = \int_V (\varepsilon_V - \varepsilon'_V) d\mathbf{V}, \quad (\text{A1})$$

$$846 \quad [\eta] = \int_V (\eta_V - \eta'_V) d\mathbf{V}, \quad (\text{A2})$$

$$847 \quad [N] = \int_V (\gamma - \gamma') d\mathbf{V}, \quad (\text{A3})$$

848 where ε_V , η_V , and γ are the densities of energy, entropy, and
849 molecules, respectively, in the real system of volume V . The
850 number of molecules n in the cluster [which enters into Eq.
851 (50)] can be defined in different ways. However, if the num-
852 ber of such molecules in the cluster (whatever its definition
853 might be) is n , the cluster's volume \mathbf{v}_n is the volume occu-
854 pied by these molecules. Thus, for example, for the energy ε_n
855 of the n -sized cluster at rest one gets

$$856 \quad \varepsilon_n = \int_{\mathbf{v}_n} \varepsilon_V d\mathbf{V}. \quad (\text{A4})$$

857 Taking into account that

$$858 \quad [\varepsilon] = \int_V (\varepsilon_V - \varepsilon'_V) d\mathbf{V} = \int_{\mathbf{v}_n} \varepsilon_V d\mathbf{V} - \varepsilon'_V \mathbf{v}_n + \int_{V-\mathbf{v}_n} (\varepsilon_V - \varepsilon'_V) d\mathbf{V}, \quad (\text{A5})$$

859 one gets

$$860 \quad \varepsilon_n = [\varepsilon] + \varepsilon'_V \mathbf{v}_n - \int_{V-\mathbf{v}_n} (\varepsilon_V - \varepsilon'_V) d\mathbf{V}, \quad (\text{A6})$$

861 where the integration is done over the volume outside the
862 drop.

863 Similar speculations can be provided for the drop en-
864 tropy η_n and number of molecules n and we get

$$865 \quad \eta_n = [\eta] + \eta'_V \mathbf{v}_n - \int_{V-\mathbf{v}_n} (\eta_V - \eta'_V) d\mathbf{V}, \quad (\text{A7})$$

$$866 \quad n = [N] + \gamma' \mathbf{v}_n - \int_{V-\mathbf{v}_n} (\gamma - \gamma') d\mathbf{V}. \quad (\text{A8})$$

867 Then, it is easy to demonstrate that the numerator of the
868 exponent in Eq. (50) for the drop being in an unstable equi-
869 librium with the neighboring vapor is equal to the work W of
870 the drop formation in the reversible Gibbs process. Indeed,
871 using Eqs. (A6)–(A8), one gets

$$872 \quad f_n^{\text{rest}} + P' \mathbf{v}_n - \mu n = \varepsilon_n - T\eta_n + P' \mathbf{v}_n - \mu n \\ 873 \quad = [\varepsilon] - T[\eta] - \mu[N] + \mathbf{v}_n (\varepsilon'_V - T\eta'_V - \mu\gamma' \\ 874 \quad + P') + \int_{V-\mathbf{v}_n} (\varepsilon'_V - T\eta'_V - \mu\gamma' - \varepsilon_V + T\eta_V \\ 875 \quad + \mu\gamma) d\mathbf{V}. \quad (\text{A9})$$

Taking into account that P' is the vapor pressure one gets¹¹ 876

$$\varepsilon'_V - T\eta'_V - \mu\gamma' + P' = 0, \quad (\text{A10}) \quad 877$$

i.e., the second term in Eq. (A9) is equal to zero. 878

Using Eq. (A10) one can write the last term in Eq. (A9) 879
as 880

$$881 \quad - \int_{V-\mathbf{v}_n} P' d\mathbf{V} - \int_{V-\mathbf{v}_n} (\varepsilon_V - T\eta_V - \mu\gamma) d\mathbf{V} \\ 882 \quad = - \int_{V-\mathbf{v}_n} P' d\mathbf{V} - \int_{V-\mathbf{v}_n} (d\varepsilon - Td\eta + \mu dN) \\ 883 \quad = \int_{V-\mathbf{v}_n} P_{\text{real}} d\mathbf{V} - \int_{V-\mathbf{v}_n} P' d\mathbf{V} \\ 884 \quad = \int_{V-\mathbf{v}_n} (P_{\text{real}} - P') d\mathbf{V}, \quad (\text{A11})$$

where P_{real} is the real pressure of the gas. The integrand 885
 $P_{\text{real}} - P'$ is the excess of the gas pressure in the neighbor- 886
hood of the drop. This excess is caused by the interaction 887
between the gas molecules being around the drop and the 888
molecules which belong to the drop. Due to the weakness of 889
the intermolecular interaction the magnitude of this integrand 890
is small enough. Neglecting the interaction between the gas 891
molecules and the drop, one can consider the last term in Eq. 892
(A9) as equal to zero. One should note that Eq. (50) was also 893
derived under the assumption that there was no interaction 894
between the gas molecules and the drop [see Eq. (47)]. 895

According to Gibbs¹¹ the reversible work of drop forma- 896
tion is equal to 897

$$W = [\varepsilon] - T[\eta] - \mu[N] \quad (\text{A12}) \quad 898$$

[i.e., to the first term in Eq. (A9)]. Thus, finally we can 899
summarize that the numerator of the exponent in Eq. (50) is 900
equal to the work of the drop formation under the ideal gas 901
mixture approximation, 902

$$f_n^{\text{rest}} + P' \mathbf{v}_n - \mu n = W. \quad (\text{A13}) \quad 903$$

The error of Eq. (A13) is equal to the value of the last 904
integral in Eq. (A11). As to this error, note that the magni- 905
tude of this integral depends not only on the potential of the 906
interaction between the vapor molecules and the n -sized 907
cluster, but on its volume \mathbf{v}_n as well. On the other hand, this 908
volume and the number n of molecules in the cluster depend 909
on the model which is chosen to define the cluster. Thus, this 910
integral is model dependent. The magnitude of this integral 911
and, as a consequence, the error of Eq. (A13) will be less in 912
the model which gives relatively large values of n and \mathbf{v}_n . 913
Recently Reiss and co-workers^{30–32} developed a new theory. 914
In terms of this theory it is possible to give a rigorous defini- 915
tion for a cluster with a very large volume involving both 916
drop and vapor (the so-called ELMD-DNT cluster). It is inter- 917
esting to note that the work of formation of this cluster is 918
strictly equal to the change of the Gibbs potential in the 919
process of the cluster formation.³² 920

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- #1 Au: Please supply Appendix title
- #2 CrossRef reports the year should be "1999" not "1998" in the reference 22 "Debenedetti, Reiss, 1998".