Contribution of van der Waals forces to the thermodynamics of a spherical particle

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The temperature Green's function of the fluctuating electromagnetic field of a spherical particle submerged in an infinite medium is found. Corrections to the thermodynamics of small particles are made on the basis of the general theory of van der Waals force.[3] These corrections depend on the size of the particle. The size dependence of the resultant surface-tension coefficient can be nonmonotonic at sizes R that are comparable with wavelengths λ_0 that are characteristic of the absorption spectra of the substances. This dependence is nonanalytic at $R \ll \lambda_0$. For particles with sizes $\sim 10^{-7}$ cm, the surface-tension coefficient can increase by $\sim 10\%$. The theory of homogeneous nucleation with account of the obtained corrections is compared qualitatively with experiment.

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The thermodynamic properties of small particles are determined in large part by the van der Waals forces associated with the fluctuation electromagnetic field. The role of these forces for plane boundaries was first investigated by E. Lifshitz.[1] In the case of particles of finite size, however, strong dependences of the thermodynamic variables can develop in the region of sizes comparable with λ_0, just as is the case for thin films.[2] In contrast with the plane interface, account of curvature leads to the appearance of size-dependent parts in the surface tension. The present paper is devoted to calculation of this contribution.

1. Using the general theory of van der Waals forces,[3] we calculate the thermodynamic quantities of a spherical particle of radius R located in an infinite medium. The medium is characterized by the dielectric permittivity $\epsilon_1(\omega)$, the particle by the permittivity $\epsilon_2(\omega)$. The chemical potential $\mu(\rho, T)$ and the stress tensor σ_{ij} in the medium can be represented with account of van der Waals forces in the form1)

$$\mu(\rho, T)=\mu_0(\rho, T)+\sigma/\rho, \tag{1}$$

$$\sigma_{ij}=-\delta_{ij}[p_0(\rho, T)+\sigma]+\sigma_{ij}', \tag{2}$$

where $\mu_0(\rho, T)$, $p_0(\rho, T)$ are the chemical potential and the pressure as functions of the density ρ and the temperature T as a uniform, unbounded medium. The terms σ and σ_{ij}' are connected with the effect of inhomogeneity on the fluctuation field and are expressed in terms of the difference of the temperature Green's functions of inhomogeneous and homogeneous media $\mathfrak{D}^0_{ij}(\mathbf{r}, \mathbf{r}'; \xi_n)$ in the following fashion:[3]

$$\sigma=\frac{T}{4\pi}\sum_{n=0}^{\infty}{}' \rho\frac{\partial\varepsilon(\mathbf{r}, i\xi_n)}{\partial\rho}\mathfrak{D}_{ll}^E(\mathbf{r}, \mathbf{r}; \xi_n), \tag{3}$$

$$\begin{aligned}\sigma_{ij}'=-\frac{T}{2\pi}\sum_{n=0}^{\infty}{}' \Big\{ &\varepsilon(\mathbf{r}, i\xi_n)\Big[\mathfrak{D}_{ij}^E(\mathbf{r}, \mathbf{r}; \xi_n)-\frac{1}{2}\delta_{ij}\mathfrak{D}_{ll}^E(\mathbf{r}, \mathbf{r}; \xi_n)\Big]\\ &+\mathfrak{D}_{ij}^H(\mathbf{r}, \mathbf{r}; \xi_n)-\frac{1}{2}\mathfrak{D}_{ll}^H(\mathbf{r}, \mathbf{r}, \xi_n)\delta_{ij}\Big\}.\end{aligned} \tag{4}$$

The prime on the summation sign indicates that the term $n = 0$ is taken with the coefficient $1/2$, while $\xi_n = 2\pi nT$,

$$\mathfrak{D}_{ij}^E(\mathbf{r}, \mathbf{r}'; \xi_n)=-\xi_n^2\mathfrak{D}_{ij}(\mathbf{r}, \mathbf{r}'; \xi_n), \tag{5}$$

$$\mathfrak{D}_{ij}^H(\mathbf{r}, \mathbf{r}'; \xi_n)=\mathrm{rot}_{il}\mathrm{rot}_{jm}'\mathfrak{D}_{lm}(\mathbf{r}, \mathbf{r}'; \xi_n). \tag{6}$$

The conditions of mechanical and thermodynamic equilibrium should be satisfied at the spherical interface:

$$\mu_{01}(\rho_1, T)+\sigma_1/\rho_1=\mu_{02}(\rho_2, T)+\sigma_2/\rho_2, \tag{7}$$

$$\begin{aligned}&p_{01}(\rho_1, T)+\sigma_1-\sigma_{rr_1}'-2\alpha_0\rho_1/R(\rho_2-\rho_1)\\ &=p_{02}(\rho_2, T)+\sigma_2-\sigma_{rr_2}'-2\alpha_0\rho_2/R(\rho_2-\rho_1)\equiv p.\end{aligned} \tag{8}$$

Here α_0 is the surface tension coefficient without account of the van der Waals forces. The indices 1 and 2 refer respectively to the medium and the sphere. Similar to what was done in[3], the terms σ_1 and σ_2, which contain $\partial\epsilon/\partial\rho$, are included in the replacement of ρ_1 and ρ_2 in (7) by functions of the pressure p_1 in the medium and p_2 in the sphere. Here, in place of (7), (8), we obtain

$$\mu_{01}(p_1, T)=\mu_{02}(p_2, T), \tag{9}$$

$$p_{1,2}=p+2\alpha_0\rho_{1,2}/R(\rho_2-\rho_1)+\sigma'_{rr1,2}. \tag{10}$$

The pressure difference and the chemical potential are connected in the usual way to the coefficient of surface tension2)

$$p_2-p_1=2\alpha/R,\ \mu_2(p_2, T)=\mu_{02}(p_{02}, T)+2\alpha/R(\rho_2-\rho_1), \tag{11}$$

where

$$\alpha=\alpha_0+R(\sigma'_{rr2}-\sigma'_{rr1})/2. \tag{12}$$

Thus, account of the fluctuation field reduces to a change in the surface tension coefficient, and for further calculations, we must find the Green's function $\mathfrak{D}_{ij}(\mathbf{r}, \mathbf{r}'; \xi_n)$. The equation for the Green's function has the form

$$\{\varepsilon(\mathbf{r}; i\xi_n)\xi_n^2\delta_{il}+\mathrm{rot}_{im}\,\mathrm{rot}_{ml}\}\mathfrak{D}_{lj}(\mathbf{r}, \mathbf{r}'; \xi_n)=-4\pi\delta(\mathbf{r}-\mathbf{r}')\delta_{ij}. \tag{13}$$

The boundary condition (in the spherical coordinates r, θ, φ) is continuity of the quantities

$$\mathfrak{D}_{\theta j},\quad \mathfrak{D}_{\varphi j},\quad \mathrm{rot}_{\theta l}\mathfrak{D}_{lj},\quad \mathrm{rot}_{\varphi l}\mathfrak{D}_{lj} \tag{14}$$

on the spherical surface, which corresponds to continuity of the tangential components of the electric and magnetic field intensities.

To solve Eq. (13), we make use of the fundamental vector spherical harmonics:[5,6]

$$\begin{aligned}&L_{jlm}(kr)=\nabla_j\psi_{lm}(kr), \quad M_{jlm}(kr)=\mathrm{rot}_{jp}x_p\psi_{lm}(kr),\\ &kN_{jlm}(kr)=\mathrm{rot}_{jp}M_{plm}(kr), \quad \psi_{lm}(kr)=j_l(kr)P_l^{|m|}(\cos\theta)e^{im\varphi},\end{aligned} \tag{15}$$

where $j_l(z) = (\pi/2z)^{1/2}J_{l+1/2}(z)$ are spherical Bessel functions $P_l^{|m|}(\cos\theta)$ the associated Lengendre polynomials. Expanding the right and left sides of Eq. (13) in series in the functions $\mathbf{L}$, $\mathbf{M}$, $\mathbf{N}$, which are orthogonal in three-dimensional space, we find the coefficients of the expansion for the Green's function of the homogeneous space[3] $\mathfrak{D}_{ij}$. Here, summation is carried out over l and m, and integration over k. The integration over k reduces to the sum of residues of the poles at $k = \pm i\xi_n \epsilon^{1/2}(i\xi_n)$, and $k = 0$. The contributions from the pole at $k = 0$ resulting from the terms containing N and L cancel one another.

Making use of the expression obtained for $\mathfrak{D}^0_{ij}$ and the boundary conditions (14), we find the Green's function $\mathfrak{D}_{ij}(\mathbf{r}, \mathbf{r}'; \xi_n)$. For $r, r' < R$,

$$\mathfrak{D}_{ij}(\mathbf{r},\mathbf{r}';\xi_n)=ik_2\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\gamma_{lm}^{-1}j_l^{-1}(z_2)h_l(z_2)\{Q_{l2}(\zeta)$$

$$\times M_{ilm}(k_2r)M^{*}_{jlm}(k_2r')+Q_{l2}(\zeta^{-1})N_{ilm}(k_2r)N^{*}_{jlm}(k_2r')\}, \tag{16}$$

where the symbol * denotes replacement of im by −im,

$$z_{1,2}=k_{1,2}R,\quad k_{1,2}=-i\xi_n\varepsilon_{1,2}^{1/2}(i\xi_n),\quad \zeta=k_1/k_2,$$

$$\gamma_{lm}=\frac{l(l+1)(l+|m|)!}{(2l+1)(l-|m|)!},\quad Q_{l2}(\zeta)=-\frac{\zeta\varphi_l(z_1)-\varphi_l(z_2)}{\zeta\varphi_l(z_1)-\psi_l(z_2)},$$

$$\varphi_l(z)=\frac{d}{dz}\ln[zh_l(z)],\quad \psi_l(z)=\frac{d}{dz}\ln[zj_l(z)],$$

$h_l(z) = (\pi/2z)^{1/2} H^{(2)}_{l+1/2}(z)$ is a Hankel function of the second kind.

For $r, r' > R$, the expression for $\mathfrak{D}_{ij}$ is obtained from (16) by the replacements $j_l(z) \rightleftarrows h_l(z)$, $1 \rightleftarrows 2$ in all the expressions.

2. We find the stress tensor σ'_{rr2} by substituting (16) in (4)—(6) and performing the summation over m. For $r < R$,

$$\sigma'_{rr2}=-\frac{Ti}{4\pi}\sum_{n=0}^{\infty}k_2^3\sum_{l=1}^{\infty}(2l+1)j_l^{-1}(z_2)h_l(z_2)j_l^2(u_2)$$

$$\cdot\frac{d\psi_l(u_2)}{du_2}[Q_{l2}(\zeta)+Q_{l2}(\zeta^{-1})],\qquad u_2=k_2r. \tag{17}$$

In the region $r > R$, the stress tensor σ'_{rr1} is obtained from (17) by the substitution given above. The surface tension is connected with the discontinuity in the stress tensor at the boundary by (12); therefore

$$\alpha=\alpha_0+\frac{RTi}{8\pi}\sum_{n=0}^{\infty}\sum_{l=1}^{\infty}(2l+1)\left\{k_1^3h_l(z_1)j_l(z_1)\frac{d\varphi_l(z_1)}{dz_1}\right.$$

$$\left.\cdot[Q_{l1}(\zeta)+Q_{l1}(\zeta^{-1})]-k_2^3h_l(z_2)j_l(z_2)\frac{d\psi_l(z_2)}{dz_2}[Q_{l2}(\zeta)+Q_{l2}(\zeta^{-1})]\right\}. \tag{18}$$

Expression (18) diverges logarithmically on summation over l. This divergence is connected with the stepwise approximation of the dielectric constant and does not depend on R. Properly conditioned calculation of this constant itself within the framework of the macroscopic theory is not possible, since a contribution to it is made by distances that are comparable with the interatomic distances, at which this theory is inapplicable.[3] However, since a contribution to the dimensionally dependent part is made by distances much greater than interatomic, we can use the simple procedure of subtraction of the divergence. For this purpose, we replace the discontinuity

$$\Delta\sigma_{rr}'=\sigma'_{rr2}(R-0)-\sigma'_{rr1}(R+0)$$

in the surface tension coefficient (12) by the difference

$$\sigma'_{rr2}(R-\Delta)-\sigma'_{rr1}(R+\Delta),$$

where $\Delta \ll R$. The expression obtained for the surface tension coefficient will be finite. Subtracting $\alpha(R)$ from it as $R \to \infty$ and setting $\Delta = 0$, we obtain the dimensionally dependent part:

$$\alpha=\alpha_\infty+\lim_{\Delta\to\infty}\left\{\frac{1}{2}R[\sigma'_{rr2}(R-\Delta)-\sigma'_{rr1}(R+\Delta)]-\alpha'(\Delta)\right\}, \tag{19}$$

$$\alpha'(\Delta)=\frac{1}{2}\lim_{R\to\infty}\{R[\sigma'_{rr2}(R-\Delta)-\sigma'_{rr1}(R+\Delta)]\}, \tag{20}$$

$$\alpha_\infty=\alpha_0+\alpha'(\Delta). \tag{21}$$

Here α_∞ is the experimentally measured coefficient of surface tension of the plane interface.

We investigate the expression for the surface tension coefficient (18) in two limiting cases:

1) "Small" particles: $R \ll \lambda_0$. Since contributions to the sum over n are made only by frequencies ξ_n for which $\epsilon(i\xi_n)$ is significantly different from unity, i.e., $\xi_n \lesssim c/\lambda_0 \ll c/R$, the arguments of the functions in (17) are small ($z_{1,2} \ll 1$), which makes it possible to expand the expression under the summation sign in (17) in a series in powers of $z_{1,2}$ and to sum over l (see Appendix). For not too high temperatures satisfying the inequality

$$\lambda_0 kT/c\hbar\ll 1, \tag{22}$$

the principal contribution to the sum is made by large n and one can go from summation over n to integration in (17).[4] Then

$$\alpha/\alpha_\infty=1+A\ln(R_1/R)+\dots, \tag{23}$$

where

$$A=\int_0^\infty f(\eta)(\varepsilon_2-\varepsilon_1)d\eta,\quad f(\eta)=\frac{c\hbar\eta^2(\varepsilon_2-\varepsilon_1)}{16\pi^2\alpha_\infty(\varepsilon_2+\varepsilon_1)},\quad \varepsilon_{1,2}=\varepsilon_{1,2}(ic\eta), \tag{24}$$

$$\ln R_1=A^{-1}\int_0^\infty f(\eta)[\varepsilon_1\ln(2\varepsilon_1^{1/2}\eta)-\varepsilon_2\ln(2\varepsilon_2^{1/2}\eta)]d\eta. \tag{25}$$

2) "Large" particles: In this case, the principal contribution to the sum over n is made by $\xi_n \gg c/R$, i.e., the arguments of the functions can be assumed to be large ($z_{1,2} \gg 1$); therefore, using the asymptotic expansions of the Bessel and Hankel functions of imaginary argument and summing over l (see Appendix), we obtain an expansion for the surface tension coefficient in powers of R^{-1}:

$$\alpha/\alpha_\infty=1+R_0/R+\dots, \tag{26}$$

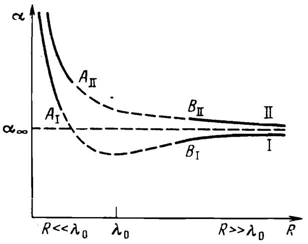
where

$$R_0=\frac{c\hbar}{16\pi^2\alpha_\infty}\int_0^\infty\eta\, d\eta\,\varepsilon_1^{1/4}\varepsilon_2^{1/4}F(\eta), \tag{27}$$

$$F(\zeta)=\frac{x(3y^2+7y+12)}{12y}+\frac{(y^2-1)}{y^{3/2}}\operatorname{Arch}(xy^{1/2})+\frac{y\Phi(\zeta)}{|x|^{1/2}(y+2)^{1/4}},$$
$$\Phi(\zeta)=\arccos(\zeta^{-1})-\operatorname{Arch}\zeta,\quad \zeta>1$$
$$\Phi(\zeta)=\operatorname{Arch}(\zeta^{-1})-\arccos\zeta,\quad \zeta<1,$$
$$x=\zeta^{1/2}-\zeta^{-1/2},\quad y=\zeta+\zeta^{-1}. \tag{28}$$

As follows from Eq. (22), in the region $R \ll \lambda_0$, the contribution to the surface tension coefficient is positive independently of the spectra of the substances ($A > 0$, $R_1 \gg R$). In the region $R \gg \lambda_0$, the sign of the coefficient R_0 is determined by the function $F(\zeta)$. It is not difficult to establish that $F(\zeta) < 0$ at $\zeta < 1$. Since $F(\zeta) = -F(\zeta^{-1})$, we have $F(\zeta) > 0$ at $\zeta > 1$. Since $\zeta = \epsilon_2^{-1/2} \le 1$ for a particle in a vacuum, then in this case $R_0 < 0$ and, conversely, for a spherical cavity in the medium, $\zeta = \epsilon^{1/2} \ge 1$; therefore $R_0 > 0$.

3. Analysis of Eqs. (23)—(28) shows that phenomenological expansions of the surface tension coefficient in powers of R^{-1} are valid only for $R \gg \lambda_0$. For $R \ll \lambda_0$, the $\alpha(R)$ dependence has a nonanalytical character. The



behavior of $\alpha(R)$ has the character shown schematically in the figure. Curve I corresponds to the case of a particle that is optically more dense than the surrounding medium, for example, a particle in a vacuum. Curve II is the opposite case—for example, a cavity in a body. In the range $R \sim \lambda_0$ (segments A_IB_I and $A_{II}B_{II}$) there is definitely a minimum in case I. Moreover, in this region, other nonmonotonicities are possible, both in case I and in case II.

The increase of the surface tension coefficient for particles with $R \sim 10$ Å can be very significant for comparison of the theory of homogeneous nucleation with experiment. In the classical theory of homogeneous nucleation (see the review of Feder et al.[7]) the quantity α^3 appears in the exponent for the nucleation rate J. A change in α by 1% changes J by a factor of about 10. Comparison of the experimental data with the classical theory with $\alpha = \alpha_\infty$ would at first appear to confirm it. However, Lothe and Pound[8] have shown that account of the change in volume of phase space due to translational and rotational motion of the nucleus leads to disagreement of theory and experiment by a factor of $\sim 10^{15}$. For agreement with the experimental data in this case, it is necessary to assume an increase in α by about 15% for a nucleus containing 50—100 particles. Although discussions are still in progress, with arguments as to both the value of the correction itself,[9-13] and the reduction of the experimental data,[7] nevertheless, an increase in the surface tension coefficient for various liquids by ~5—20% is recognized as a necessity for agreement between theory and experiment.[14-15]

The difficulty of estimating $\Delta\alpha(R)$ according to (23) is that $\epsilon(\omega)$ has been poorly studied in the range of frequencies $\omega \gtrsim 10^{16}$ sec^{-1}.[16] However, we shall attempt to make the corresponding estimates for water, using for $\epsilon(i\omega)$ the formula

$$\varepsilon(i\omega) = 1 + B[1 + (\omega/\omega_0)^2]^{-1}, \quad B \ll 1. \tag{29}$$

Substituting (29) into (24) and (25) and integrating over η, we get

$$\Delta\alpha/\alpha_\infty \approx q\hbar\omega_0^3 B^2/128\pi c^2 \alpha_\infty, \quad q \gg 1. \tag{30}$$

Setting B = 0.5, q = 2, α_∞ = 75 erg/cm^2, we find that an effect of ~ 10% requires that $\omega_0 \sim 10^{17}$ sec^{-1}. Taking into account the conditional character of Eq. (29), such an ω_0 could be regarded as intermediate between the characteristic frequencies of strong absorption for water, $\omega_1 = 1.9 \times 10^{16}$ sec^{-1} and $\omega_2 = 1.5 \times 10^{18}$ sec^{-1}.[16]

It must be kept in mind, of course, that one can use Eq. (23) only qualitatively in this case, since $\omega_0 R/c \lesssim 1/3$. As is seen from the drawing, for values of R in the vicinity of a change of sign of $\Delta\alpha$, the values of both J and $|dJ/dR|$ will be smaller than for $\alpha = \alpha_\infty$, which possibly (with account of the Lothe-Pound correction) corresponds to the experimental results of Allen and Kassner.[17] At high degrees of supersaturation, the dependence of J on the supersaturation will be stronger than predicted by the classical theory.

We note that the increase in the surface tension coefficient of small particles can also be a consequence of other mechanisms, for example, the mechanism considered by Fletcher[18] of disordering in the surface layer in the transition from large to small drops.

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APPENDIX

We make use of the representation of the Bessel and Handel functions in series form (see[19]); then the expansion in powers of z for the functions $j_l(z)$ and $h_l(z)$ with $l \neq 0$ has the form

$$h_l(z) = \frac{i\pi^{1/2}(-1)^l}{2\Gamma(1/2 - l)}\left(\frac{z}{2}\right)^{-l-1}\left[1 + \frac{z^2}{2(2l-1)} + \ldots\right],$$

$$j_l(z) = \frac{\pi^{1/2}}{(2l+1)\Gamma(l+1/2)}\left(\frac{z}{2}\right)^l\left[1 - \frac{z^2}{2(2l+3)} + \ldots\right]. \tag{A.1}$$

Using the expansion (A.1), we can easily find the expansion of the functions $\varphi_l(z)$, $\psi_l(z)$, $d\varphi_l(z)/dz$, $d\psi_l(z)/dz$, after substitution of which in (19) we get for α:

$$\alpha = \alpha_0 - \frac{T}{2\pi}\sum_{n=0}^{\infty}\xi_n^2(\varepsilon_2 - \varepsilon_1)^2\sum_{l=1}^{\infty}\left(1 - \frac{\Delta}{R}\right)^{2l+1} \cdot \frac{l(l+1)}{(2l-1)(2l+3)[l\varepsilon_2 + \varepsilon_1(l+1)]} + \ldots, \tag{A.2}$$

where $\epsilon_{1,2} \equiv \epsilon_{1,2}(i\xi_n)$. Accurate to within a constant that is independent of R, and to terms $\sim\Delta/R$, the expression (A.2), after summation over l, reduces to the form

$$\alpha = \alpha_0 + \frac{T}{8\pi}\ln\left(\frac{2\Delta}{R}\right)\sum_{n=0}^{\infty}\xi_n^2\frac{(\varepsilon_2 - \varepsilon_1)^2}{(\varepsilon_2 + \varepsilon_1)} + \ldots \tag{A.3}$$

As is seen from (A.3), α diverges logarithmically as $\Delta \to 0$.

To perform the subtraction procedure of (19), we first find the expansion in powers of R^{-1}. Taking into account the asymptotic representation of the Bessel and Hankel functions of imaginary argument at large arguments[19], we obtain the following expansions of $j_l(z)$ and $h_l(z)$ in powers of z^{-1};

$$j_l(-ix) = \frac{(-i)^l\exp(-p\beta + x\operatorname{ch}\beta)}{2x\operatorname{ch}^{1/2}\beta}\left(1 - \frac{a_1}{x\operatorname{ch}\beta} + \ldots\right),$$

$$h_l(-ix) = -\frac{(i)^l\exp(p\beta - x\operatorname{ch}\beta)}{x\operatorname{ch}^{1/2}\beta}\left(1 + \frac{a_1}{x\operatorname{ch}\beta} + \ldots\right), \tag{A.4}$$

$$p = l + 1/2, \quad \operatorname{sh}\beta = p/x, \quad a_1 = -1/8 + 5/24\operatorname{th}\beta.$$

From the asymptotics behavior of (A.4), we find that of the functions $\varphi_l(z)$, $\varphi_l(z)$, $d\varphi_l(z)/dz$, and $d\varphi_l(z)/dz$. Substituting the resultant asymptotic forms in (19), and replacing the summation over l by integration (the sum differs from the integral by the term $\sim x^{-3}$) we get after simple but cumbersome transformations

$$\alpha = \alpha_0 + \alpha'(\Delta) + \frac{T}{32\pi R}\sum_{n=0}^{\infty}\xi_n^2\varepsilon_2^{1/2}\int_0^{\infty} y\,dy\{y[f_3^3 f_1 + f_4^3 f_5^2) f_1 f_2^2 - 3(\zeta^2 - 1)^{-1}(f_3^2 + f_4^2 f_5)(f_2^{5/2} + \zeta^2 f_1^{5/2}) + (f_1^{3/2} - f_2^{3/2})[y(f_1 + f_2) - \zeta f_1 f_2 f_3 f_4 f_5]\}, \tag{A.5}$$

where

$$f_1 = (\zeta^2 + y)^{-1}, \quad f_2 = (1 + y)^{-1}, \quad f_3 = f_1^{-1/2} - f_2^{-1/2},$$

$$f_4=f_1^{-1/2}-\zeta^2 f_2^{-1/2}, \qquad f_5=[1-(1+\zeta^2)(1+y)]^{-1},$$

$$\alpha'(\Delta)=\frac{T}{16\pi}\sum_{n=0}^{\infty}\xi_n{}^2\varepsilon_2\int_0^{\infty} y\,dy\exp[-2\Delta\xi_n(\varepsilon_2 y)^{1/2}]f_1f_2(f_3{}^2+f_4{}^2f_5). \qquad (A.6)$$

Under the integral sign in (A.5), we went immediately to the limit $\Delta \to 0$.

Integration over y leads to formulas (26)—(28). The value of $\alpha'(\Delta)$ is computed with logarithmic accuracy in Δ and has the form

$$\alpha'(\Delta)\approx\frac{T}{8\pi}\sum_{n=0}^{\infty}\xi_n{}^2\frac{(\varepsilon_2-\varepsilon_1)}{(\varepsilon_2+\varepsilon_1)}[\varepsilon_2\ln(2\varepsilon_2^{1/2}\xi_n\Delta)-\varepsilon_1\ln(2\varepsilon_1^{1/2}\xi_n\Delta)]. \qquad (A.7)$$

We used this formula in the subtraction procedure (19)—(21) to remove the divergence in the surface tension coefficient.

Note added in proof (April 23, 1975). Our definition of $\alpha(R)$ corresponds to a small change in the thermodynamic potential on a small change in the size of the particle without any change in its shape (after subtraction of the volume terms). The transition to the surface tension coefficient ordinarily used in nucleation theory, $\gamma(R)$ $(\Omega = \Omega_0 + \gamma(R)S)$ [12] is easily accomplished by integrating the differential equation

$$d\gamma(R)/dR+2\gamma(R)/R=2\alpha(R)/R$$

with the boundary condition $\alpha(\infty) = \gamma(\infty)$. Using the asymptotes (23), (26), we can easily establish that the behavior of $\gamma(R)$ is similar to the behavior of $\alpha(R)$.

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1) We have used $\hbar = c = k = 1$ everywhere, with the exception of the final formulas; k = Boltzmann's constant, $\hbar$ = Planck's constant, c = velocity of light.

2) We define α as $(\partial\Omega/\partial S)_{T\mu}$, where Ω is the thermodynamic potential, S the area of the interface. [4]

3) The functions L, N are not orthogonal if they are considered on a sphere. [5]

4) For $\lambda_0 \sim 10^{-4}$ cm, the inequality (22) is valid for $T \ll 300°K$.

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