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On the Macroscopic Theory of Temperature-Dependent van der Waals Forces

Barry W. Ninham,[1,2] V. Adrian Parsegian,[1] and
George H. Weiss[1]

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We give a simple derivation of the van der Waals free energy of interaction between two semiinfinite media, including effects of nonzero temperature and retardation. The method, an extension of one used by van Kampen and co-workers at the short-distance and low-temperature limits, considers the free energy of electromagnetic surface modes in the region between the two media. The result is the same as derived by Lifshitz and co-workers using Green's function techniques.

KEY WORDS: Free energy; electromagnetic interactions; optical properties; dielectric properties.

In a variety of applications,(1–4) it is usually assumed that the van der Waals interaction between macroscopic bodies is due primarily to electromagnetic correlations at ultraviolet frequencies. Typically,(2) the macroscopic theory due to Lifshitz,(5) which automatically takes into account all interaction frequencies, is reduced to a limiting form similar to that of the old Hamaker–London(6) theory. That limiting case explicitly ignores temperature effects intrinsic to microwave and infrared fluctuation frequencies. It can also ignore the essential nonadditivity of long-range forces in condensed media.

Recent studies(7–9) suggest that there are biologically important cases of interaction in which the lower frequencies predominate even in the regime of small

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[1] Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland.

[2] Permanent address: Department of Applied Mathematics, University of New South Wales, Kensington, N.S.W., Australia.

distances. In these cases the van der Waals forces are temperature-dependent, and retardation effects are important only for ultraviolet frequencies.

The general result due to Lifshitz has been obtained by Dzyaloshinskii *et al.*(10) via a difficult and lengthy argument involving the use of Green's function techniques of quantum field theory. Our aim in this note is to rederive Lifshitz's expression by an heuristic and intuitive method which avoids these complications. The method is an extension of that used by van Kampen *et al.*,(11) who recovered the special case of the general result which holds at zero temperature when retardation effects are ignored.

Consider two semiinfinite media of material 1 bounding a third planar medium of thickness l, material 2, as in Fig. 1. The interaction between the outer media can be regarded as a sum of free-energy contributions from allowed surface modes of the system, i.e., from the normal mode frequencies of the equivalent set of harmonic oscillators. The contribution from a single normal mode ω_j is $kT \ln[\sinh(\beta\hbar\omega_j/2)]$, where $\beta = 1/(kT)$, k is the Boltzmann constant, T is temperature, and $2\pi\hbar$ is Planck's constant. We therefore consider the enumeration of the ω_j for the system shown, under the assumption that the material dielectric susceptibilities differ, $\epsilon_1(\omega) \neq \epsilon_2(\omega)$, but the magnetic susceptibilities are the same, $\mu_1 = \mu_2$.

We seek solutions of the wave equations, harmonic in time such that we can write for the electric and magnetic fields

$$\mathbf{E} = \sum_{\omega} \mathbf{E}_{\omega} e^{-i\omega t}, \qquad \mathbf{H} = \sum_{\omega} \mathbf{H}_{\omega} e^{-i\omega t} \tag{1}$$

The allowed frequencies in the summation satisfy the wave equations

$$\nabla^2(\mathbf{E}_{\omega}, \mathbf{H}_{\omega}) + (\epsilon\omega^2/c^2)(\mathbf{E}_{\omega}, \mathbf{H}_{\omega}) = 0 \tag{2}$$

together with

$$\nabla \cdot \mathbf{E}_{\omega} = 0, \qquad \nabla \cdot \mathbf{H}_{\omega} = 0 \tag{3}$$

These are found by the conditions that the components of $(\mathbf{E}_{\omega}, \mathbf{H}_{\omega})$, E_x, E_y, ϵE_z,

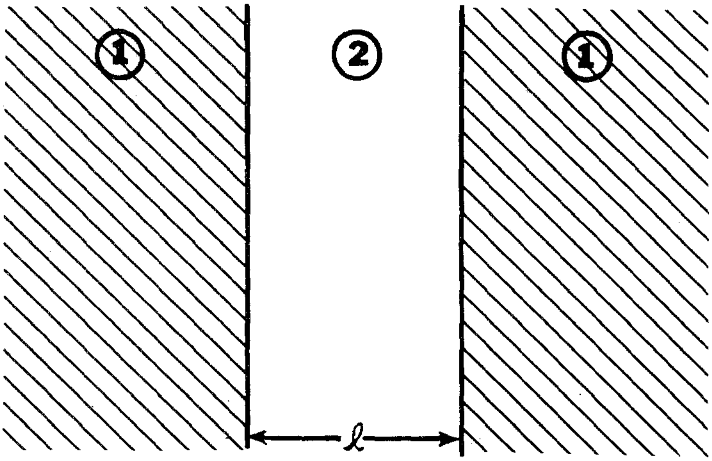

Fig. 1

H_x, H_y, μH_z, be continuous at the material boundaries. (We take the material boundaries parallel to the x, y plane at $z = 0$ and $z = l$.)

For each component of $\mathbf{E}_\omega$ and $\mathbf{H}_\omega$ we assume the form

$$f(z)\, e^{i(ux+vy)}.$$

The six functions $f(z)$ satisfy

$$f''(z) - \rho^2 f(z) = 0 \tag{4}$$

where $\rho^2 = u^2 + v^2 - [\omega^2\epsilon(\omega)/c^2] = r^2 - [\omega^2\epsilon(\omega)/c^2]$ and r is the (real) component of the wave vector parallel to the slab of material 2.

These equations (4) have exponential solutions

$$f = Ae^{\rho z} + Be^{-\rho z} \tag{5}$$

where A and B are constants of integrations. Taking account of the fact that only surface modes are of interest, we find that the normal modes $\{\omega_i\}$ are roots of either of two dispersion relations,

$$\begin{aligned} D_1(\omega; \rho) &= 1 - \Delta^2 e^{-2\rho_2 l} = 0 \\ D_2(\omega; \rho) &= 1 - \bar{\Delta}^2 e^{-2\rho_2 l} = 0 \end{aligned} \tag{6}$$

where

$$\bar{\Delta} = (\rho_2\epsilon_1 - \rho_1\epsilon_2)/(\rho_2\epsilon_1 + \rho_1\epsilon_2), \qquad \Delta = (\rho_2 - \rho_1)/(\rho_2 + \rho_1) \tag{7}$$

The requirement $\mathrm{Re}(\rho_2) > 0$ implies that $r \geqslant (\omega/c)\,\mathrm{Re}(\epsilon^{1/2})$ in what follows. The two dispersion relations in Eq. (6) can be combined into the single relation

$$D = D_1 D_2 = 0 \tag{8}$$

The free energy of interaction, denoted $G(l, T)$, is formally given by

$$G(l, T) = (1/2\pi) \int_0^\infty [G_l(r) - G_\infty(r)]\, r\, dr \tag{9}$$

where we integrate over all wave vectors r and

$$G_l(r) = kT \sum_j \ln[\sinh(\beta\hbar\omega_j/2)] \tag{10}$$

in which the summation goes over all of the real roots of Eq. (8). In order to evaluate the sum over the ω_j, we make use of the identity

$$\sum g(\omega_j) = (1/2\pi i) \int_C g(\omega)[1/D(\omega)][dD(\omega)/d\omega]\, d\omega \tag{11}$$

where the contour C includes the relevant zeros of D, and excludes poles of $g(\omega)$. The functions $g(z)$ and $D(z)$ are assumed to be analytic in order for Eq. (11) to hold.

Since $g(\omega) = \ln[\sinh(\beta\hbar\omega/2)]$ has branch points, it is convenient to expand it as

$$g(\omega) = (\hbar\omega/2) - \sum_{n=1}^{\infty} (1/n)\, e^{-n\beta\hbar\omega} \tag{12}$$

and consider each term separately. Proceeding formally, we choose the contour in Eq. (11) from $-i\infty$ to $+i\infty$ along the imaginary axis and around the right half-plane along a semicircular path whose radius goes to infinity [excluding any zeros of $D(\omega)$ on the imaginary axis].

Since $\epsilon(|\omega|) \to 1$ as $|\omega| \to \infty$, $D(|\omega|) = 1$ on the semicircle and we can write

$$G_l(r) = (1/2\pi i) \int_{\infty}^{-\infty} g(i\xi)\{d[\ln D(i\xi; r)]/d\xi\}\, d\xi \tag{13}$$

and an integration by parts yields

$$G_l(r) = (\hbar/2) \sum_j \omega_j + (\hbar/2\pi) \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \cos(n\beta\hbar\xi) \ln D_l(i\xi; r)\, d\xi$$
$$- (i\hbar/2\pi) \sum_{n=1}^{\infty} \int_{0}^{\infty} \sin(n\beta\hbar\xi) \ln[D_l(i\xi; r)/D_l(-i\xi; r)]\, d\xi \tag{14}$$

The summation over cosine terms can be carried out by interchanging summation and integration and making use of the identity

$$\sum_{n=1}^{\infty} \cos nx = \pi \sum_{n=-\infty}^{\infty} \delta(x - 2\pi n) - \tfrac{1}{2} \tag{15}$$

When the delta functions are substituted into the integrals, the integrations can be carried out leading to the formula

$$(\hbar/2) \sum_j \omega_j + (\hbar/2\pi) \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} [\cos(n\beta\hbar\xi)] \ln D_l(i\xi; r)\, d\xi$$
$$= (kT/2) \sum_{n=-\infty}^{\infty} \ln D_l(i\xi_n\,; r) \tag{16}$$

where

$$\xi_n = (2\pi kT/\hbar)\, n \tag{17}$$

so that

$$G_l(r) = (kT/2) \sum_{n=-\infty}^{\infty} [\ln D_l(i\xi_n\,; r)]$$
$$- (i\hbar/2\pi) \sum_{n=1}^{\infty} \int_{0}^{\infty} \sin(n\beta\hbar\xi) \ln[D_l(i\xi; r)/D_l(-i\xi; r)]\, d\xi \tag{18}$$

When the dielectric constants have the form

$$\epsilon(\omega) = 1 + \sum_j [c_j/(\omega_j^2 - \omega^2)] \tag{19}$$

i.e., are functions of ω^2 only, the second term in Eq. (18) is identically zero by symmetry and Eq. (18) reduces to

$$G_l(r) = kT \sum_{n=0}^{\infty}{}' \ln D(i\xi_n\,; r) \tag{20}$$

where the prime indicates that the $n = 0$ term is multiplied by 1/2. This result is easily shown to be equivalent to the form derived from Lifshitz's expression for the force by Ninham and Parsegian(7)

$$G(l, T) = (kT/8\pi l^2) \sum_{n=0}^{\infty}{}' \{2\xi_n l[\epsilon_2(i\xi_n)]^{1/2}/c\}^2$$
$$\times \int_1^{\infty} p \ln\{[1 - \Delta^2 \exp(-2p\xi_n l\epsilon_2^{1/2}/c)][1 - \bar{\Delta}^2 \exp(-2p\xi_n l\epsilon_2^{1/2}/c)]\}\, dp \tag{21}$$

where

$$\begin{gathered}\bar{\Delta} = (s - p)/(s + p), \qquad \Delta = (s\epsilon_2 - p\epsilon_1)/(s\epsilon_2 + p\epsilon_1) \\ s = [p^2 - 1 + (\epsilon_1/\epsilon_2)]^{1/2}\end{gathered} \tag{22}$$

The correspondence is established by replacing ρ_2 by $\xi_n[\epsilon_2(i\xi_n)]^{1/2}\, p/c$ in the nth term of Eq. (20), from which it follows that $\rho_1 = \{\xi_n[\epsilon_2(i\xi_n)]^{1/2}/c\}\, s$. When the r integration is carried out from 0 to ∞, corresponding to p going from 1 to ∞, the result is that given in Eq. (21).

A more general form for the $\epsilon_i(\omega)$, $i = 1, 2$, includes Debye relaxation terms,

$$\epsilon(\omega) = 1 + \sum_m [c_m/(1 - i\omega\tau_m)] + \sum_s [c_s/(\omega_s{}^2 - \omega^2)] \tag{23}$$

where the c_m and τ_m are positive real constants. In general, the microwave region is well separated from regions described by the Lorentz relaxation ($\omega_s\tau_m \gg 1$ for all s, m; e.g., for water, $\omega_s\tau_m \gtrsim 10^3$). However, the terms in $(1 - i\omega\tau_m)^{-1}$ violate the symmetry of $D(i\xi)$ in ξ as well as cause zeros and poles in $D(i\xi)$ on the $-\xi$ axis. The second term in Eq. (18) is not obviously zero. Rather than attempt to integrate this second term directly, it is simpler first to rewrite $D(\omega)$ preserving its zeros on the real axis.

Note that the $(1 - i\omega\tau_m)^{-1}$ terms add no new real positive roots to the original sum of Eq. (10). In the microwave region, we have

$$\epsilon(\omega) = C + \sum_m [c_m/(1 - i\omega\tau_m)] \tag{24}$$

where C is a real, positive constant. In order for $D(\omega)$ to have a zero, it is necessary for $[(\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)]^2$ to be real and $\geqslant 1$. This condition cannot be satisfied by the form of Eq. (23). Further, above the microwave region, the Debye terms are negligible and do not affect the roots, due to ordinary Lorentz dispersion.

We may therefore vary the τ_m without affecting the physically essential property of $D(\omega)$. In particular, consider the limit $\tau_m \to \infty$ for $\xi \neq 0$. In this limit, the ratio

$D(i\xi)/D(-i\xi)$ is unity, so that the integral in question is zero and may be neglected. We again obtain the final formula (19).

The great advantage of using the van Kampen surface-mode analysis is the triviality of generalizing the simplest result for the interaction of two semiinfinite media. One need only evaluate an appropriate dispersion relation $D(\omega) = 0$ for multiple-layer and nonplanar systems by solution of the wave equations for surface modes. Extension to triple films,(12) multilayers,(9) and membrane interaction is immediate. Solutions for nonplanar geometries require straightforward solution of the relevant wave equations.

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