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Addendum

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# STATISTICAL THEORY OF THE DIELECTRIC CONSTANT OF AN IMPERFECT GAS

Allan N. Kaufman and Kenneth M. Watson

April 7, 1961

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Allan N. Kaufman and Kenneth M. Watson

Physics Department and Lawrence Radiation Laboratory
University of California
Berkeley and Livermore, California

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We may develop a more explicit expression for $\alpha_2$, for use in Eq. (6.35). From Eqs. (6.29) and (4.10), and the definition of the linkage operator, we have

$$\underset{\sim}{\alpha}'_2 = \int d^3R \left[ -\frac{1}{2}\gamma^{-2} \mathrm{Tr}(2\pi i)^{-1} \int dw\, e^{-\beta w}(w-H^2)^{-1} \underset{\approx}{p}^{(2)}(w-H^2)^{-1} \underset{\approx}{p}^{(2)} - \underset{\sim}{\alpha}_1 \right], \quad (1)$$

since the $\underset{\sim}{\alpha}_1$ term subtracts off the unlinked diagrams. Note that $H^2$ is the $\underset{\sim}{R}$-dependent two-molecule Hamiltonian in the absence of a field, $\underset{\sim}{R}$ being the vector between the two molecular centers of mass. To obtain $\underset{\sim}{\alpha}_2$ from (6.33), we also need $b_2$, which we quote from paper I, Eq. (4.16):

$$b_2 = \int d^3R \left[ \frac{1}{2}\gamma^{-2} \mathrm{Tr} \exp(-\beta H^2) - \frac{1}{2} \right]. \quad (2)$$

The subtraction of $2b_2 \underset{\sim}{\alpha}_1$ from $\underset{\sim}{\alpha}'_2$ then yields $\underset{\sim}{\alpha}_2$:

$$\underset{\sim}{\alpha}_2 = \int d^3R \left[ -\frac{1}{2}\gamma^{-2} \mathrm{Tr}(2\pi i)^{-1} \int dw\, e^{-\beta w}(w-H^2)^{-1} \underset{\approx}{p}^{(2)}(w-H^2)^{-1} \underset{\approx}{p}^{(2)} \right.$$

$$\left. - \underset{\sim}{\alpha}_1 \gamma^{-2} \mathrm{Tr} \exp(-\beta H^2) \right]. \quad (3)$$

By analogy to Eq. (4.10), we see that the polarizability of the two-molecule system for fixed $\underset{\sim}{R}$ is

$$\underset{\sim}{\alpha}_2(\underset{\sim}{R}) = - [\mathrm{Tr}\ \exp(-\beta H^2)]^{-1}\ \mathrm{Tr}(2\pi i)^{-1} \int dw\ e^{-\beta w}\ (w-H^2)^{-1}\ \underset{\sim}{p}^{(2)}(w-H^2)^{-1}\ \underset{\sim}{p}^{(2)} \quad . \tag{4}$$

Thus $\underset{\sim}{\alpha}_2$ reduces to the expression:

$$\underset{\sim}{\alpha}_2 = \gamma^{-2} \int d^3\underset{\sim}{R}\ [\ \tfrac{1}{2}\ \underset{\sim}{\alpha}_2(\underset{\sim}{R}) - \underset{\sim}{\alpha}_1]\ \mathrm{Tr}\ \exp\ [-\beta H^2\ (\underset{\sim}{R})]\ . \tag{5}$$

We note that

$$\gamma^2 = \mathrm{Tr}\ \exp\ [-\beta H^2\ (\infty)]\ , \tag{6}$$

since $H^2(\infty)$ is just $h_1 + h_2$. We therefore introduce a quantity $\Phi\ (\underset{\sim}{R})$ defined by

$$\exp\ [-\beta\ \Phi(\underset{\sim}{R})] = \gamma^{-2}\ \mathrm{Tr}\ \exp\ [-\beta H^2(\underset{\sim}{R})]\ ; \tag{7}$$

it is the free energy* of the two-molecule system as a function of $\underset{\sim}{R}$, with the zero of energy taken at $R = \infty$. Equation (5) then becomes

$$\underset{\sim}{\alpha}_2 = \int d^3R\ e^{-\beta\Phi(\underset{\sim}{R})}\ [\ \tfrac{1}{2}\ \underset{\sim}{\alpha}_2\ (\underset{\sim}{R}) - \underset{\sim}{\alpha}_1\ ]\ ; \tag{8}$$

this formula states that $\underset{\sim}{\alpha}_2$ is obtained from the increase in polarizability per molecule of the two-molecule system over that of an isolated molecule, integrated over all $\underset{\sim}{R}$ with a weight given by the low-density correlation function.

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* R. W. Zwanzig, Phys. Rev, 106, 13 (1957). This paper shows that $\Phi(\underset{\sim}{R})$ is the effective intermolecular interaction energy in the adiabatic approximation.

The most general form of $\underset{\sim}{\alpha}_2(\underset{\sim}{R})$ is

$$\underset{\sim}{\alpha}_2(\underset{\sim}{R}) = 2\alpha_{\parallel}(R)\,\hat{\underset{\sim}{R}}\,\hat{\underset{\sim}{R}} + 2\alpha_{\perp}(R)(\underset{\sim}{I} - \hat{\underset{\sim}{R}}\,\hat{\underset{\sim}{R}}) \ . \tag{9}$$

Here $\hat{\underset{\sim}{R}}$ is the unit vector from the center of mass of one molecule to that of the other, while $2\alpha_{\parallel}$ and $2\alpha_{\perp}$ are the eigenvalues of the tensor $\underset{\sim}{\alpha}_2(\underset{\sim}{R})$. If the two-molecule system is placed in an external field parallel to the line of centers, $\alpha_{\parallel}(R)$ is the polarizability per molecule at fixed R; similarly, $\alpha_{\perp}(R)$ gives the response for a transverse field.

We substitute (9) into (8) and integrate over solid angle; using the fact that $\underset{\sim}{\Phi}$ depends only upon R, we obtain

$$\underset{\sim}{\alpha}_2 = 4\pi \int_0^{\infty} R^2\, dR\, e^{-\beta\underset{\sim}{\Phi}(R)}\left[\frac{1}{3}\alpha_{\parallel} + \frac{2}{3}\alpha_{\perp} - \alpha_1\right]\underset{\sim}{I} \ , \tag{10}$$

yielding the scalar $\alpha_2$ for Eq. (6.35).