GENERALIZED KEESOM POTENTIAL *

by

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ABSTRACT

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A field theoretic approach is used to derive general expressions
for the adiabatic interaction between two rotating dipolar systems,
whose temperatures may differ. The results, which are expressed in
terms of the dipole moments, moments of inertia and temperatures of
the two systems are valid, in second order approximation, over the
whole range of temperatures including the region where quantum effects
are important. The classical limit reduces to the Keesom potential
for equal temperatures. When the temperatures are different the
classical potential can take on positive (repulsive) values as well
as negative (attractive) values, depending on the temperature
difference and ratio of temperature to moment of inertia of the two
systems; for large temperature differences the potential is always
repulsive. The general equations are analyzed and the quantum-
statistical implications underlying the theory are discussed.

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I. Introduction

When two rotating dipole moments are at close distance from each other, their correlated motion gives rise to a potential of interaction, the classical limit of which is the well-known Keesom potential[1]. The Keesom force is one of the constituents of the van der Waals interaction and plays an important role in problems involving polar molecules.

The purpose of this work is twofold: a) to generalize the Keesom potential so as to include quantum effects; b) to extend the treatment to the interaction between molecules which are at different temperatures, that is, molecules which have distributions characteristic of different temperatures and which interact adiabatically.

The inclusion of quantum effects in the Keesom potential is not merely of academic interest. As has been pointed out before[2,3,4], most polar molecules have dipole moments of such magnitude that for ordinary temperatures the classical approximation is not quite valid. The generalization of the Keesom potential to different temperatures is also of practical interest. In certain types of scattering experiments it is often convenient - and sometimes necessary - to maintain different temperatures for the scattering gas and for the beam molecules. Rothe and Bernstein[3] and Schumacher, Bernstein and Rothe[4] have described such a series of experiments; the conditions were such that the adiabatic interaction approximation was approximately valid. A formula designed to cope with this situation has been suggested[4] for the classical limit, but a detailed

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general theory has not been formulated.

The approach to be followed here will be based on the field technique described in an earlier paper[5]. This technique applies to systems obeying classical as well as quantum mechanics. Moreover, this method views the overall interaction as resulting from two separate events, namely, the polarization of molecule 1 by the electromagnetic fluctuations of molecule 2 and vice versa; the mechanism for generalizing the results to different temperatures is, therefore, present from the start.

II. Procedure

Consider two rotating molecules (electrical systems) at temperatures T_1 and T_2. As a working model, we could suppose that the two systems are immersed in separate heat baths each of which is adiabatically enclosed: electrical energy can be transferred, but not heat. Let the complex susceptibilities associated with the rotational motion of systems "1" and "2" be denoted respectively by

$$\hat{\beta}_1(\omega) = \beta_1'(\omega) - i\,\beta_1''(\omega) \quad \text{and} \quad \hat{\beta}_2(\omega) = \beta_2'(\omega) - i\,\beta_2''(\omega)$$

These susceptibilities are functions of the molecular properties of the systems and also of the temperatures. The general treatment outlined in Section II of Ref. 5 applies also to the present case and yields

$$\phi_{or}^{(2)} = W_{2\to1} + W_{1\to2} \tag{II-1}$$

where

$$W_{2\to1} = -\frac{3\hbar}{\pi\,r_{12}^6}\int_0^\infty \beta_1'(\omega)\,\beta_2''(\omega)\,\coth\!\left(\frac{\hbar\omega}{2\,kT_2}\right)d\omega \tag{II-2}$$

$$W_{1\to2} = -\frac{3\hbar}{\pi\,r_{12}^6}\int_0^\infty \beta_2'(\omega)\,\beta_1''(\omega)\,\coth\!\left(\frac{\hbar\omega}{2\,kT_1}\right)d\omega \tag{II-3}$$

Here, $\phi_{or}^{(2)}$ is the generalized pair potential, associated with the rotational motion of the dipole moments (orientation effect); $W_{2 \to 1}$ denotes the work of polarization of molecule 1 by the fluctuations of molecule 2; $W_{1 \to 2}$ is the work of polarization of molecule 2 by the electrical fluctuations of molecule 1; and r_{12} is the internuclear separation, assumed fixed. These expressions have general validity within the framework of the dipolar approximation, in which retardation effects have been neglected, and apply over the whole range of temperatures. Hence, in a formal sense, the theory is complete and the generalized potential can be calculated from a knowledge of the frequency-dependence of the susceptibility functions. The determination of complex susceptibilities is, in general, very difficult and requires detailed knowledge of the wave-functions of the systems. In the case of rigid rotors, however, a representation can easily be obtained (see Appendix) and yields the following general expressions[6]:

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \int_0^\infty dy \, \frac{y(1 - e^{-\hbar y/kT})}{y^2 - \omega^2} \sum_{j=0}^\infty e^{-j(j+1)\hbar\omega^o/kT} (j+1) \delta(y + \omega^o_{j,j+1}) \quad \text{(II-4)}$$

and

$$\beta''(\omega) = \frac{\pi\mu^2}{3\hbar Q} (1 - e^{-\hbar\omega/kT}) \sum_{j=0}^\infty e^{-j(j+1)\hbar\omega^o/kT} (j+1) \delta(\omega + \omega^o_{j,j+1}) \quad \text{(II-5)}$$

where

$$\mu = e r_0 \qquad \text{(dipole moment)}$$

$$Q = \sum_{j=0}^{\infty} (2j+1) \, e^{-j(j+1)\hbar\omega^0/kT} \qquad \text{(rotational partition function)}$$

$$\text{(II-6)}$$

$$\omega^0 = \frac{\hbar}{2I} \qquad \text{("natural" frequency)}$$

$$\omega^0_{j,j+1} = \frac{E_j - E_{j+1}}{\hbar} = -2(j+1)\,\omega^0 \qquad \text{(transition frequency)}$$

The E_j's are the unperturbed rotational energy states; I is the moment of inertia; and the bar across the integral sign in Eq.(II-4) denotes the Cauchy principle value. The imaginary part of the susceptibility, $\beta''(\omega)$, has also a negative branch (see Appendix) which has not been included in Eq. (II-5) inasmuch as integration over ω in the free energy expression requires only positive values of ω .

The introduction of (II-4) and (II-5) into Eq. II-2 yields

$$W_{2\to1} = -\frac{2\mu_1^2\mu_2^2}{3r_{12}^6\hbar Q_1 Q_2}\left\{\int_0^\infty d\omega\left(1 - e^{-\hbar\omega/kT_2}\right)\coth\left(\frac{\hbar\omega}{2kT_2}\right)\right.$$

$$\times\sum_{j'=0}^\infty e^{-j'(j'+1)\hbar\omega_2^0/kT_2}\,(j'+1)\,\delta(\omega-\omega_{j',j'+1}^0)\int_0^\infty dy\,\frac{y(1-e^{-\hbar y/kT_1})}{y^2-\omega^2}$$

$$\left.\times\sum_{j=0}^\infty e^{-j(j+1)\hbar\omega_1^0/kT_1}\,(j+1)\,\delta(y-\omega_{j,j+1}^0)\right\}$$

<div align="right">(II-7)</div>

and a similar expression for $W_{1\to2}$. The subscript 1 and quantum numbers j serve to characterize molecule "1"; molecule "2" is characterized by the subscript 2 and quantum numbers j'. On integrating out the variables y and ω we obtain an expression which, when added to the analogous expression for $W_{1\to2}$, gives

$$\phi_{or}^{(2)} = -\frac{2\mu_1^2\mu_2^2}{3r_{12}^6\hbar Q_1 Q_2}\left[\left\{\sum_{j'=0}^{\infty}{}' e^{-j''(j'+1)\hbar\omega_2^0/kT_2}\left(1-e^{-2(j'+1)\hbar\omega_2^0/kT_2}\right)(j'+1)\coth\frac{2(j'+1)\hbar\omega_2^0}{2kT_2}\right.\right.$$

$$\times\sum_{j=0}^{\infty}{}' e^{-j(j+1)\hbar\omega_1^0/kT_1}\left(1-e^{-2(j+1)\hbar\omega_1^0/kT_1}\right)\frac{2(j+1)^2\omega_1^0}{\left[2(j+1)\omega_1^0\right]^2-\left[2(j'+1)\omega_2^0\right]^2}\Bigg\}$$

$$+\left\{\sum_{j=0}^{\infty} e^{-j(j+1)\hbar\omega_1^0/kT_1}\left(1-e^{-2(j+1)\hbar\omega_1^0/kT_1}\right)(j+1)\coth\frac{2(j+1)\hbar\omega_2^0}{2kT_2}\right.$$

$$\left.\left.\times\sum_{j'=0}^{\infty}{}' e^{-j''(j'+1)\hbar\omega_2^0/kT_2}\left(1-e^{-2(j'+1)\hbar\omega_2^0/kT_2}\right)\frac{2(j'+1)^2\omega_2^0}{\left[2(j'+1)\omega_2^0\right]^2-\left[2(j+1)\omega_1^0\right]^2}\right\}\right]$$

<div align="right">(II-8)</div>

The apostrophe behind the summation signs serves to denote that
states for which the denominator vanishes are to be omitted. This
restriction is a consequence of the principal value requirement
of the preceding equations.

Another form, equivalent to (II-8), is obtained on noting
that, for example, $\coth\dfrac{2(j+1)\hbar\omega_1^0}{2kT_1}$

$$= \left(1+e^{-2(j+1)\hbar\omega_i^0/kT_1}\right)\Big/\left(1-e^{-2(j+1)\hbar\omega_i^0/kT_1}\right)$$

and $\ e^{-j(j+1)\hbar\omega_i^0/kT_1}\left(1\pm e^{-2(j+1)\hbar\omega_i^0/kT_1}\right)$

$$= e^{-j(j+1)\hbar\omega_i^0/kT_1}\pm e^{-(j+1)(j+2)\hbar\omega_i^0/kT_1}$$

The result is

$$\phi_{or}^{(2)} = -\frac{2\mu_1^2\mu_2^2}{3r_{12}^6 \hbar Q_1 Q_2}\left[\left\{\sum_{j'=0}^{\infty}\left(e^{-j'(j'+1)\hbar\omega_2^o/kT_2} + e^{-(j'+1)(j'+2)\hbar\omega_2^o/kT_2}\right)(j'+1)\right.\right.$$

$$\times \left.\sum_{j=0}^{\infty}{}'\left(e^{-j(j+1)\hbar\omega_1^o/kT_1} - e^{-(j+1)(j+2)\hbar\omega_2^o/kT_2}\right)(j+1)\frac{2(j'+1)\omega_1^o}{[2(j+1)\omega_1^o]^2-[2(j'+1)\omega_2^o]^2}\right\}$$

$$-\left\{\sum_{j=0}^{\infty}\left(e^{-j(j+1)\hbar\omega_1^o/kT_1} + e^{-(j+1)(j+2)\hbar\omega_1^o/kT_1}\right)(j+1)\right.$$

$$\times \left.\left.\sum_{j'=0}^{\infty}{}'\left(e^{-j'(j'+1)\hbar\omega_2^o/kT_2} - e^{-(j'+1)(j'+2)\hbar\omega_2^o/kT_2}\right)(j'+1)\frac{2(j'+1)\omega_2^o}{[2(j+1)\omega_1^o]^2-[2(j'+1)\omega_2^o]^2}\right\}\right]$$

$$(\text{II-9})$$

Still another general formula can be derived by combining
terms appearing in the first of the curly brackets of II-9 with
corresponding terms of the second of the curly brackets. For
example, one set of terms, appearing within the first curly
brackets, is

$$T_{\{\}_1} = \sum_{j'=0}^{\infty} e^{-j'(j'+1)\hbar\omega_2^o/kT_2}(j'+1)\sum_{j=0}^{\infty}{}'\, e^{-j(j+1)\hbar\omega_1^o/kT_1}(j+1)\frac{2(j'+1)\omega_1^o}{[2(j+1)\omega_1^o]^2-[2(j'+1)\omega_2^o]^2}.$$

$$(\text{II-10})$$

We drop the restriction on the second summation, which has the
effect of introducing terms for which $(j+1)\omega_1^o = (j'+1)\omega_2^o$
and correct for this effect by subtracting out these singular
terms, e.g.

$$\sum_{j'=0}^{\infty}( )\sum_{j=0}^{\infty}{}'( ) = \sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}( )( ) - \sum_{j'}\sum_{j}( )( )$$
$$(j+1)\omega_1^0 = (j'+1)\omega_2^0$$

The order of the summation is now unimportant, and we can combine
Eq. (II-10) with the analogous expression, having the same
exponentials, of the second curly brackets; the result is

$$T_{\{\}_1} + T_{\{\}_2} = \sum_{j=0}^{\infty}\sum_{j'=0}^{\infty} e^{-j(j+1)\hbar\omega_1^0/kT_1} \; e^{j'(j'+1)\hbar\omega_2^0/kT_2}$$

$$\times \frac{(j+1)(j'+1)}{2(j+1)\omega_1^0 + 2(j'+1)\omega_2^0} \qquad\qquad \text{(II-11)}$$

The singular terms are of opposite sign and cancel. Similarly,
when we perform the same operation on the terms involving the
exponentials

$$e^{-j'(j+1)\hbar\omega_1^0/kT_1} = ( )_1$$

and

$$e^{-(j'+1)(j'+2)\hbar\omega_2^0/kT_2} = ( )_2 \qquad ,$$

we get

$$\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty} ( )_1( )_2 \frac{(j+1)(j'+1)}{2(j+1)\omega_1^0 - 2(j'+1)\omega_2^0}$$

$$- \sum_{j}\sum_{j'} ( )_1( )_2 \frac{(j+1)(j'+1)}{2(j'+1)\omega_1^0 - 2(j'+1)\omega_2^0}$$
$$(j+1)\omega_1^0 = (j'+1)\omega_2^0$$

The singular terms do not cancel here but must be excluded from the
double summation. The complete expression for the potential is

$$\phi_{or}^{(2)} = -\frac{2\mu_1^2\mu_2^2}{3r_{12}^6 \hbar Q_1 Q_2}\left[\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}{}'(j+1)(j'+1)\right.$$

$$\times\left\{\frac{e^{-j(j+1)\hbar\omega_1^o/kT_1}\,e^{-j'(j'+1)\hbar\omega_2^o/kT_2} - e^{-(j+1)(j+2)\hbar\omega_1^o/kT_1}e^{-(j'+1)(j'+2)\hbar\omega_2^o/kT_2}}{2(j+1)\omega_1^o + 2(j'+1)\omega_2^o}\right\}$$

$$\left.+\left\{\frac{e^{-j(j+1)\hbar\omega_1^o/kT_1}\,e^{-(j'+1)(j'+2)\hbar\omega_2^o/kT_2} - e^{-(j+1)(j+2)\hbar\omega_1^o/kT_1}\,e^{-j'(j'+1)\hbar\omega_2^o/kT_2}}{2(j+1)\omega_1^o - 2(j'+1)\omega_2^o}\right\}\right]$$

(II-12)

where the prime behind the summation signs again denotes that
states for which the terms become singular are to be excluded –
thus, none in the first brackets and states for which

$$(j+1)\omega_1^o = (j'+1)\omega_2^o$$ in the second. Equation (II-12) can be
given a simple physical interpretation, reference to which is
made in the Discussion.

Classical Limit

The classical (high temperature) limit can be derived from Eq. II-8 by expanding the hyperbolic contangent functions and the functions $e^{-2(j+1)\hbar\omega_1^0/kT_1}$ and $e^{-2(j'+1)\hbar\omega_2^0/kT_2}$ in power series or, more directly, from Eq. II-12 by the expansion of the latter two functions. If we then replace all summations by integrations, we obtain to first order

$$\phi_{or}^{(2)} = -\frac{4\mu_1^2\mu_2^2}{3\,r_{12}^6\hbar} \cdot \frac{1}{\left(\int_0^\infty (2j+1)e^{-j(j+1)\hbar\omega_1^0/kT_1}\,dj\right)} \cdot \frac{1}{\left(\int_0^\infty (2j'+1)e^{-j'(j'+1)\hbar\omega_2^0/kT_2}\,dj'\right)}$$

$$\times \frac{\hbar}{\omega_1^0 kT_1} \cdot \frac{\hbar}{\omega_2^0 kT_2}\left[\frac{kT_2}{\hbar}\int_0^\infty dj' \int_0^\infty dj\, e^{-j(j+1)\hbar\omega_1^0/kT_1}\, e^{-j'(j'+1)\hbar\omega_2^0/kT_2}\right.$$

$$\times [(j+1)\omega_1^0]^3[(j'+1)\omega_2^0]\Big/\{[(j+1)\omega_1^0]^2 - [(j'+1)\omega_2^0]^2\}$$

$$+ \frac{kT_1}{\hbar}\int_0^\infty dj \int_0^\infty dj'\, e^{-j(j+1)\hbar\omega_1^0/kT_1}\, e^{-j'(j'+1)\hbar\omega_2^0/kT_2}$$

$$\left.\times [(j'+1)\omega_2^0]^3[(j+1)\omega_1^0]\Big/\{[(j'+1)\omega_1^0]^2 - [(j+1)\omega_2^0]^2\}\right] \qquad \text{(II-13)}$$

We next make the substitutions $(j+1)\omega_1^0 = p$, $(j'+1)\omega_2^0 = q$, $a = \hbar/\omega_1^0 kT_1$ and $b = \hbar/\omega_2^0 kT_2$ and replace the integrals in the denominator by $kT_1/\hbar\omega_1^0$ and $kT_2/\hbar\omega_2^0$ which are the classical values of the rotational partition function;

the result is

$$\phi_{or}^{(2)} = -\frac{4\mu_1^2\mu_2^2}{3\,r_{12}^6} \cdot \frac{ab}{kT_1 T_2} \left\{ T_2 \int_{\omega_2^0}^{\infty} dq \int_{\omega_1^0}^{\infty} dp\, e^{-\left(ap^2 - \frac{\hbar p}{kT_1}\right)} e^{-\left(bq^2 - \frac{\hbar q}{kT_2}\right)} \frac{p^3 q}{p^2 - q^2} \right.$$

$$\left. + T_1 \int_{\omega_1^0}^{\infty} dp \int_{\omega_2^0}^{\infty} dq\, e^{-\left(ap^2 - \frac{\hbar p}{kT_1}\right)} e^{-\left(bq^2 - \frac{\hbar q}{kT_2}\right)} \frac{q^3 p}{q^2 - p^2} \right\}$$

$$(II\text{-}14)$$

We drop the linear terms in the exponents as these terms would, upon expansion, contribute inverse powers in T_1 and T_2 which are of a higher order and switch to the variables x and y defined by $x^2 = ap^2$ and $y^2 = bq^2$; we get

$$\phi_{or}^{(2)} = -\frac{4\mu_1^2\mu_2^2}{3\,r_{12}^6\,kT_1 T_2} \left\{ T_2 \int_{\delta_2}^{\infty} dy \int_{\delta_1}^{\infty} dx\, e^{-(x^2 + y^2)} \frac{x^3 y}{x^2 - \frac{a}{b} y^2} \right.$$

$$(II\text{-}15)$$

$$\left. + T_1 \int_{\delta_1}^{\infty} dx \int_{\delta_2}^{\infty} dy\, e^{-(x^2 + y^2)} \frac{y^3 x}{y^2 - \frac{b}{a} x^2} \right\}$$

The lower limits of integration δ_1 and δ_2 are respectively

$$\delta_1 = a^{1/2} \omega_1^0 = \left(\hbar \omega_1^0 / kT_1\right)^{1/2}$$

and

$$\delta_2 = b^{1/2} \omega_2^0 = \left(\hbar \omega_2^0 / kT_2\right)^{1/2}$$

and approach zero in the limit of $T_1 \rightarrow \infty$ and $T_2 \rightarrow \infty$.

Thus, if we change these integration limits to zero and introduce

the cylindrical coordinates $x = r\cos\theta$, $y = r\sin\theta$ (and

$dxdy = r\,dr\,d\theta$) we get for the first double integral

$$A = \int_0^\infty dy \int_0^\infty dx\, e^{-(x^2+y^2)} \frac{x^3 y}{x^2 - \frac{a}{b} y^2} = \int_0^\infty dr\, e^{-r^2} r^3 \int_0^{\pi/2} d\theta\, \frac{\cos^3\theta \sin\theta}{\cos^2\theta - \frac{a}{b}\sin^2\theta}$$

$$= -\frac{1}{2}\frac{b}{a+b} \int_0^1 \frac{t^3}{\varkappa^2 - t^2}\,dt \tag{II-16}$$

where $t = \cos\theta$ and $\varkappa^2 = a/a+b$. (The factor of ½ is the value

of the integral over the r coordinate.) Evaluation of the

principal value integral, which according to the definition can

be written as

$$\int_0^1 = \lim_{\varepsilon \to 0}\left[\int_0^{\varkappa - \varepsilon} + \int_{\varkappa + \varepsilon}^1 \right]$$

presents no special difficulties and yields

$$\int_0^1 \frac{t^3}{\varkappa^2 - t^2}\,dt = -\left[\frac{1}{2} + \frac{1}{2}\varkappa^2 \ln \frac{1 - \varkappa^2}{\varkappa^2} \right] \tag{II-17}$$

Substitution into (II-16) gives

$$A = \frac{1}{4}\cdot\frac{b}{a+b}\left[1 + \frac{a}{a+b} \ln \frac{b}{a} \right] \tag{II-18}$$

A similar analysis shows that the second double integral of

Eq. (II-15) produces

$$B = \int_0^\infty dx \int_0^\infty dy \, e^{-(x^2+y^2)} \frac{y^3 x}{y^2 - \frac{b}{a}x^2}$$

(II-19)

$$= \frac{1}{4} \cdot \frac{a}{a+b}\left[1 + \frac{b}{a+b} \ln \frac{a}{b}\right]$$

Since

$$a = \hbar/\omega_1^0 kT_1 = (2/k)(I_1/T_1)$$

and

$$b = \hbar/\omega_2^0 kT_2 = (2/k)(I_2/T_2)$$

we can express A and B in terms of the more convenient ratios

$$f_1 = T_1/I_1 \qquad \text{and} \quad f_2 = T_2/I_2 \qquad \text{which, when substituted}$$

into Eq. (II-15), yield the final expression

$$\phi_{or}^{(2)} = -\frac{\mu_1^2 \mu_2^2}{3kT_1 T_2 r_{12}^6}\left\{T_2 \frac{f_1}{f_1+f_2} + T_1 \frac{f_2}{f_1+f_2} + (T_2 - T_1)\frac{f_1 f_2}{(f_1+f_2)^2} \ln \frac{f_1}{f_2}\right\}$$

(II-20)

We may consider three special cases:

i) $T_1 = T_2 = T$. The usual Keesom potential is then recovered[7]:

$$\phi_{or}^{(2)} = -\frac{\mu_1^2 \mu_2^2}{3kT r_{12}^6}$$

(II-21)

ii) $f_1 = f_2$ or $T_{1}/I_1 = T_{2}/I_2$. The potential then becomes

$$\phi_{or}^{(2)} = -\frac{\mu_1^2 \mu_2^2}{3k\, r_{12}^6} \cdot \frac{T_1 + T_2}{2T_1 T_2} \tag{II-22}$$

This potential corresponds to the average potential energy proposed by Schumacher, Bernstein and Rothe[4].

    iii) $I_1 = I_2$. The potential takes the form

$$\phi_{or}^{(2)} = -\frac{2\mu_1^2 \mu_2^2}{3k(T_1 + T_2)\, r_{12}^6} \left\{ 1 + \frac{T_2 - T_1}{T_1 + T_2} \ln\left(\frac{T_1}{T_2}\right)^{1/2} \right\} \tag{II-23}$$

III. Discussion

The general behavior of the double-temperature potentials differs markedly from the ordinary single-temperature potential and the meaning of some of the results is not clear to the author. The logarithmic term appearing in the classical formula (Eq. II-20) can be either positive, zero or negative and in the latter case may actually overshadow the nonlogarithmic terms – in which case the potential becomes repulsive. For two rotors with equal moments of inertia (Eq. II-23), the turning point occurs when the temperatures satisfy the condition

$$\ln \xi^{1/2} = \coth \ln \xi^{1/2} \tag{III-1}$$

where ξ is either T_1/T_2 or T_2/T_1. This happens when $\ln \xi$ is approximately 2.40 or $\xi = 11.0$. Thus, in case of molecules with identical moments of inertia the potential becomes repulsive when T_1/T_2 or T_2/T_1 exceeds the value 11.0.

The appearance of repulsive interaction terms is, from a field-theoretic point of view, not so surprising. In the Fourier decomposition of $W_{2 \to 1}$ and $W_{1 \to 2}$ (Eqs. II-2 and II-3) both positive and negative terms occur: the positive terms of, say, $W_{2 \to 1}$ are the result of polarization of system "1" by impulses of system "2" of such high frequencies that they exceed the "natural" frequency, $\omega_1^0 = \hbar/2I_1$, of system "1". But in the overall expression for the free energy the positive terms always cancel in the classical limit when the temperatures are equal;

this is not the case when the temperatures differ.

Direct comparison between the present results and those obtained by a purely statistical approach is not possible at present since an _ab initio_ statistical theory has not yet been formulated. Nonetheless, by relabelling some of the quantities appearing in the basic equations, it is possible to transform these equations in such a way that their statistical implications become clearly discernable. Thus, if we replace in Eq. (II-12) all frequencies by corresponding energies, e.g.

$$\exp\left\{-j(j+1)\hbar\omega_i^0/kT_1\right\} = \exp\left\{-E_j^{(1)}/kT_1\right\} \quad,$$

$$\exp\left\{-(j+1)(j+2)\hbar\omega_i^0/kT_1\right\} = \exp\left\{-E_{j+1}^{(1)}/kT_1\right\} \quad,$$

$$-2(j+1)\omega_i^0 = \left(E_j^{(1)} - E_{j+1}^{(1)}\right)/\hbar \quad,$$

etc. and make the following substitutions (see Appendix)

$$\frac{1}{3}(j+1)\mu_1^2 = \sum_{m=-j}^{j}\left|e\,z_{j,m;j+1,m}^{(1)}\right|^2 = \left|e\,z_{j,j+1}^{(1)}\right|^2 \qquad \text{(III-2)}$$

and

$$\frac{1}{3}(j'+1)\mu_2^2 = \sum_{m=-j'}^{j'}\left|e\,z_{j'm;j'+1,m}^{(2)}\right|^2 = \left|e\,z_{j',j'+1}^{(2)}\right|^2$$

we get

$$\phi_{or}^{(2)} = - \frac{6}{r_{12}^6 Q_1 Q_2} \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty}{}' \left| e z_{j,j+1}^{(1)} \right|^2 \left| e z_{j',j'+1}^{(2)} \right|^2$$

$$\times \left\{ \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} - e^{-E_{j+1}^{(1)}/kT_1} e^{-E_{j'+1}^{(2)}/kT_2}}{\left(E_{j+1}^{(1)} + E_{j'+1}^{(2)} \right) - \left(E_j^{(1)} + E_{j'}^{(2)} \right)} \right.$$

$$\left. + \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{j'+1}^{(2)}/kT_2} - e^{-E_{j+1}^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2}}{\left(E_{j+1}^{(1)} + E_{j'}^{(2)} \right) - \left(E_j^{(1)} + E_{j'+1}^{(2)} \right)} \right\} \qquad \text{(III-3)}$$

Further, by changing the suffices $j+1$ and $j'+1$ to i and i' respectively, we can also write

$$\phi_{or}^{(2)} = - \frac{6}{r_{12}^6 Q_1 Q_2} \left\{ \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} \left| e z_{j,j+1}^{(1)} \right|^2 \left| e z_{j',j'+1}^{(2)} \right|^2}{\left(E_{j+1}^{(1)} + E_{j'+1}^{(2)} \right) - \left(E_j^{(1)} + E_{j'}^{(2)} \right)} \right.$$

$$+ \sum_{i=1}^{\infty} \sum_{i'=1}^{\infty} \frac{e^{-E_i^{(1)}/kT_1} e^{-E_{i'}^{(2)}/kT_2} \left| e z_{i,i-1}^{(1)} \right|^2 \left| e z_{i',i'-1}^{(2)} \right|^2}{\left(E_{i-1}^{(1)} + E_{i'-1}^{(2)} \right) - \left(E_i^{(1)} + E_{i'}^{(2)} \right)}$$

$$+ \sum_{j=0}^{\infty} \sum_{i'=1}^{\infty}{}' \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{i'}^{(2)}/kT_2} \left| e z_{j,j+1}^{(1)} \right|^2 \left| e z_{i',i'-1}^{(2)} \right|^2}{\left(E_{j+1}^{(1)} + E_{i'-1}^{(2)} \right) - \left(E_j^{(1)} + E_{i'}^{(2)} \right)} \qquad \text{(III-4)}$$

$$\left. + \sum_{i=1}^{\infty} \sum_{j'=0}^{\infty}{}' \frac{e^{-E_i^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} \left| e z_{i,i-1}^{(1)} \right|^2 \left| e z_{j',j'+1}^{(2)} \right|^2}{\left(E_{i-1}^{(1)} + E_{j'+1}^{(2)} \right) - \left(E_i^{(1)} + E_{j'}^{(2)} \right)} \right\}$$

or, more compactly

$$\phi_{or}^{(2)} = -\frac{6}{r_{12}^6 Q_1 Q_2}\sum_{j,\eta}\sum_{j',\eta'}{}' \frac{e^{-E_j^{(1)}/kT_1}\, e^{-E_{j'}^{(2)}/kT_2}\,|ez_{j,\eta}^{(1)}|^2\,|ez_{j',\eta'}^{(2)}|^2}{(E_\eta^{(1)}+E_{\eta'}^{(2)})-(E_j^{(1)}+E_{j'}^{(2)})} \qquad \text{(III-5)}$$

where j and j' run from 0 to ∞ and $\eta = j \pm 1 \geqslant 0$ and
$\eta' = j' \pm 1 \geqslant 0$. This expression exhausts all possible transitions
between the states of system "1" and all possible transitions
between the states of system "2" . We note that $e^{-E_j^{(1)}/kT_1}/Q_1$
is simply the probability, $P_j^{(1)}$, that molecule "1" be found in
the unperturbed energy level $E_j^{(1)}$ and that $e^{-E_{j'}^{(2)}/kT_2}/Q_2$ is the
probability that molecule "2" is in the unperturbed rotational
state $E_{j'}^{(2)}$. Also, since an expression like $|z_{j,\eta}|^2$ is invariant
of the axis of quantization[8], we can replace the quantity

$$\left(6/r_{12}^6\right)|ez_{j,\eta}^{(1)}|^2\,|ez_{j',\eta'}^{(2)}|^2$$

by

$$\left(e^4/r_{12}^6\right)\left[|x_{j,\eta}^{(1)}|^2\,|x_{j',\eta'}^{(2)}|^2+|y_{j,\eta}^{(1)}|^2\,|y_{j',\eta'}^{(2)}|^2+4|z_{j,\eta}^{(1)}|^2\,|z_{j',\eta'}^{(2)}|^2\right]$$

which is the square of the matrix element of the interaction
Hamiltonian

$$\mathcal{H}' = \left(e^2/r_{12}^3\right)\left[x_1 x_2 + y_1 y_2 - 2z_1 z_2\right]$$

Thus, if we use the notation $\mathcal{H}'_{jj',mm';\eta\eta',mm'}$ to define
the matrix elements between initial and final states of the

combined systems "1" and "2" and (in analogy with (III-2) write

$$\sum_{m=-j}^{j}\sum_{m'=-j'}^{j'} |\mathcal{H}'_{jj',mm';\eta\eta',mm'}|^2 = |\mathcal{H}'_{jj',\eta\eta'}|^2$$

we obtain

$$\phi_{or}^{(2)} = -\sum_{j,\eta}\sideset{}{'}\sum_{j',\eta'} \rho_j^{(1)}\rho_{j'}^{(2)} \frac{|\mathcal{H}'_{jj',\eta\eta'}|^2}{(E_\eta^{(1)} + E_{\eta'}^{(2)}) - (E_j^{(1)} + E_{j'}^{(2)})} \qquad \text{(III-6)}$$

The meaning of this result is now clear: it is the expression for the quantum-mechanical second order perturbation energy representing the interaction between all possible states of system "1" with all possible states of system "2", each state being weighted by a Boltzmann factor having a temperature characteristic of the system to which the state belongs.

This analysis by no means provides statistical proof of the validity of the basic equations derived here; it merely suggests that the underlying assumptions on which the equations are based are, from a quantum-statistical point of view, plausible.

<u>Appendix:</u>   <u>Frequency-Dependent Susceptibility of a Rotating Dipole</u>

Below is a brief derivation of the formulas for $\beta''(\omega)$ and $\beta'(\omega)$.
A more extensive discussion and analysis of the functional behavior
of the complex susceptibility will be presented in a later paper.

Consider a rotating dipole, of moment $\mu = e\, r_0$,
responding to an external field (in the z -direction) of
frequency ω . The imaginary part of the response function can
be derived by application of the formal expression [9]

$$\beta''(\omega) = \frac{(\pi/\hbar)(1 - e^{-\hbar\omega/kT}) \sum_p \sum_q e^{-E_p/kT} |e\, z_{pq}|^2 \delta(\omega + \omega_{pq})}{\sum_p e^{-E_p/kT}} \quad \text{(A-1)}$$

where p and q are different quantum states of the unperturbed
system and $\omega_{pq} = (E_p - E_q)/\hbar$. The zeroth order wave
function of a rigid rotor is

$$\psi_{jm}^{(0)} = \sqrt{\frac{(2j+1)(j-m)!}{4\pi\,(j+m)!}}\; P_j^m(\cos\theta)\, e^{im\phi} \quad \text{(A-2)}$$

where the $P_j^m(\cos\theta)$ are the associated Legendre functions and m
can take on any integral value between -j and j. This wave-
function produces the matrix elements

$$z_{j,m;j',m'} = \left\langle P_j^m(\cos\theta)\, e^{-im\phi}\; r_0 \cos\theta\; P_{j'}^{m'}(\cos\theta)\, e^{im'\phi} \right\rangle$$

which have the following properties

$$Z_{j,m;j',m'} = \frac{r_0}{\sqrt{2j+3}} \sqrt{\frac{(j+1-m)(j+1+m)}{2j+1}} \quad \text{if } j'=j+1 \text{ and } m=m'$$

$$= \frac{r_0}{\sqrt{2j-1}} \sqrt{\frac{(j-m)(j+m)}{2j+1}} \quad \text{if } j'=j-1 \text{ and } m=m'$$

$$\text{(A-3)}$$

$$= 0 \qquad\qquad \text{otherwise.}$$

If we let E_{jm} denote the energy of a state characterized by the quantum numbers j and m and $\omega^0_{jm,j'm'}$ the transition frequency $\left(E_{jm} - E_{j'm'}\right)/\hbar$, we obtain

$$\beta''(\omega) = \frac{\pi\left(1 - e^{-\hbar\omega/kT}\right)}{\hbar Q} \sum_{j=0}^{\infty} \sum_{m=-j}^{j} e^{-E_{jm}/kT}$$

$$\times \left\{ \left| e Z_{j,m;j+1,m} \right|^2 \delta\left(\omega + \omega^0_{jm,(j+1)m}\right) + \left| e Z_{j,m;j-1,m} \right|^2 \delta\left(\omega + \omega^0_{jm,(j-1)m}\right) \right\}$$

$$\text{(A-4)}$$

where

$$Q = \sum_{j=0}^{\infty} \sum_{m=-j}^{j} e^{-E_{jm}/kT}$$

Since, however, the energies are independent of the quantum number m, i.e.

$$E_{jm} = E_j = j(j+1)\hbar^2/2I = j(j+1)\hbar\omega^0 \qquad ,$$

we can write

$$\beta''(\omega) = \frac{\pi(1-\bar{e}^{\hbar\omega/kT})}{\hbar Q}\left\{\sum_{j=0}^{\infty} e^{-E_j/kT}\sum_{m=-j}^{j}\left|e\, z_{j,m;j+1,m}\right|^2 \delta(\omega+\omega^o_{j,j+1})\right.$$

$$\left.+\sum_{j=1}^{\infty} e^{-E_j/kT}\sum_{m=-j}^{j}\left|e\, z_{j,m;j-1,m}\right|^2 \delta(\omega+\omega^o_{j,j-1})\right\}$$

(A-5)

where

$$Q = \sum_{j=0}^{\infty}(2j+1)\, e^{-j(j+1)\hbar\omega^o/kT} \qquad, \quad \omega^o_{j,j+1} = -2(j+1)\omega^o$$

and

$$\omega^o_{j,j-1} = 2j\omega^o \quad .$$

It may be noted that for every value of j except j = 0,
there is a positive and negative value for $\beta''(\omega)$. Summation
over m produces

$$\sum_{m=-j}^{j}\left|e\, z_{j,m;j+1,m}\right|^2 = e^2 r_o^2 \sum_{m=-j}^{j}\frac{(j+1)^2-m^2}{(2j+3)(2j+1)}$$

$$= \mu^2\left\{\frac{(j+1)^2(2j+1)-\frac{1}{3}(2j+1)j(j+1)}{(2j+3)(2j+1)}\right\}$$

(A-6)

$$= \frac{1}{3}\mu^2(j+1)$$

and

$$\sum_{m=-j}^{j} |e\, z_{j,m; j-1,m}|^2 = e^2 r_0^2 \sum_{m=-j}^{j} \frac{j^2 - m^2}{(2j+1)(2j-1)}$$

$$= \mu^2 \left\{ \frac{j^2(2j+1) - \frac{1}{3}(2j+1)j(j+1)}{(2j+1)(2j-1)} \right\} \qquad \text{(A-7)}$$

$$= \frac{1}{3} \mu^2 j$$

where use has been made of the relation[8]

$$\sum_{m=-j}^{j} m^2 = \frac{1}{3}(2j+1)j(j+1)$$

Substitution of (A-6) and (A-7) into (A-5), gives the final result (see also comments in footnote ref. 6):

$$\beta''(\omega) = \frac{\pi \mu^2 (1 - e^{-\hbar\omega/kT})}{3\hbar Q} \left\{ \sum_{j=0}^{\infty} e^{-j(j+1)\hbar\omega^0/kT} (j+1)\, \delta(\omega + \omega^0_{j,j+1}) \right.$$

$$\left. + \sum_{j=1}^{\infty} e^{-j(j+1)\hbar\omega^0/kT} j\, \delta(\omega + \omega^0_{j,j-1}) \right\} \qquad \text{(A-8)}$$

The real part of the susceptibility can be obtained immediately

from A-8 (using the positive branch only!) by application of the

Kramers-Kronig relation

$$\beta'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{y\beta''(y)}{y^2 - \omega^2} \, dy$$

The result is

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \int_0^\infty dy \, \frac{y}{y^2 - \omega^2} \left(1 - e^{-\hbar y/kT}\right) \sum_{j=0}^\infty e^{-j(j+1)\hbar\omega^0/kT} (j+1) \delta(y + \omega^0_{j,j+1})$$

(A-9)

The latter can also be written as a sum over discrete states

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \sum_{j=0}^\infty{}' \frac{2(j+1)^2 \omega^0 \left(1 - e^{-2(j+1)\hbar\omega^0/kT}\right) e^{-j(j+1)\hbar\omega^0/kT}}{[2(j+1)\omega^0]^2 - \omega^2}$$

(A-10)

or

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \sum_{j=0}^\infty{}' \frac{2(j+1)^2 \omega^0 \left(e^{-j(j+1)\hbar\omega^0/kT} - e^{-(j+1)(j+2)\hbar\omega^0/kT}\right)}{[2(j+1)\omega^0]^2 - \omega^2}$$

(A-11)

where the prime on the summation sign denotes that states for which

$$2(j+1)\omega^0 = \omega$$ are to be omitted.

As a special case, we find that the static susceptibility

$$\beta'(0) = \beta(0) = \frac{2\mu^2}{3\hbar Q} \cdot \frac{1}{2\omega^0} = \frac{\mu^2}{3\hbar\omega^0 \sum_{j=0}^\infty (2j+1) e^{-j(j+1)\hbar\omega^0/kT}}$$

(A-12)

which reduces to the Debye-Langevin formula $\beta(0) = \mu^2/3kT$

upon replacing the summation over j in the denominator of A-12

by an integration.

References

1. W. H. Keesom, Z. Physik $\underline{22}$, 129 (1921).

2. R. H. Cole, J. Chem. Phys. $\underline{39}$, 2602 (1963).

3. E. W. Rothe and R. B. Bernstein, J. Chem. Phys. $\underline{31}$, 1619 (1959).

4. H. Schumacher, R. B. Bernstein and E. W. Rothe, J. Chem. Phys. $\underline{33}$, 584 (1960).

5. B. Linder, J. Chem. Phys. $\underline{40}$, 2003 (1964).

6. These expressions are strictly valid for heteronuclear diatomic molecules. For homonuclear diatomic molecules, summation has to be restricted to either even or odd values of j depending on the symmetry properties of the electronic states and of the nuclear spin states. This has the effect of reducing the number of allowed rotational states roughly by a factor of two, which can be corrected for by introducing a "symmetry" number (of 2) leaving the summations otherwise unrestricted. Since both numerator and denominator have to be divided by the same symmetry number, the final expressions remain unaltered.

7. We wish to emphasize that $\phi_{or}^{(2)}$ is a free energy; it differs from the energy (in the statistical sense, i.e. the interaction Hamiltonian averaged over all configurations) by a factor of $\frac{1}{2}$. (See ref. 5.)

8. J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, 1932; Chapter VII.

9. L. D. Landau and E. M. Lifshitz, "Statistical Physics", Pergamon Press (London-Paris), 1958; S 123.

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