

## GENERALIZED KEESOM POTENTIAL \*

by

Bruno Linder

Department of Chemistry, The Florida State University,  
Tallahassee, Florida

ABSTRACT

28854

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.

*Author*

- - - - -  
\* This research was carried out in part under Grant NsG-275-62 from the National Aeronautics and Space Administration.

## 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<sup>1</sup>. 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<sup>2,3,4</sup>, 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<sup>3</sup> and Schumacher, Bernstein and Rothe<sup>4</sup> 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<sup>4</sup> for the classical limit, but a detailed

general theory has not been formulated.

The approach to be followed here will be based on the field technique described in an earlier paper<sup>5</sup>. 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

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

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

$$\phi_{\text{or}}^{(2)} = W_{2 \rightarrow 1} + W_{1 \rightarrow 2} \quad (\text{II-1})$$

where

$$W_{2 \rightarrow 1} = -\frac{3\hbar}{\pi r_{12}^6} \int_0^{\infty} \beta_1'(\omega) \beta_2''(\omega) \coth\left(\frac{\hbar\omega}{2kT_2}\right) d\omega \quad (\text{II-2})$$

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

Here,  $\phi_{or}^{(2)}$  is the generalized pair potential, associated with the rotational motion of the dipole moments (orientation effect);  $W_{2 \rightarrow 1}$  denotes the work of polarization of molecule 1 by the fluctuations of molecule 2;  $W_{1 \rightarrow 2}$  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<sup>6</sup>:

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

and

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

where

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

$$Q = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\hbar\omega^0/kT} \quad (\text{rotational partition function}) \quad (\text{II-6})$$

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

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

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  $\omega$  in the free energy expression requires only positive values of  $\omega$ .

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

$$W_{2 \rightarrow 1} = -\frac{2\mu_1^2 \mu_2^2}{3r_{12}^6 \hbar Q_1 Q_2} \left\{ \int_0^\infty d\omega (1 - e^{-\hbar\omega/kT_2}) \coth\left(\frac{\hbar\omega}{2kT_2}\right) \right. \\ \times \sum_{j'=0}^{\infty} e^{-j'(j'+1)\hbar\omega_2^0/kT_2} (j'+1) \delta(\omega - \omega_{j',j'+1}^0) \int_0^\infty dy \frac{y(1 - e^{-\hbar y/kT_1})}{y^2 - \omega^2} \\ \left. \times \sum_{j=0}^{\infty} e^{-j(j+1)\hbar\omega_1^0/kT_1} (j+1) \delta(y - \omega_{j,j+1}^0) \right\}$$

(II-7)

and a similar expression for  $W_{1 \rightarrow 2}$ . 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  $\omega$  we obtain an expression which, when added to the analogous expression for  $W_{1 \rightarrow 2}$ , gives

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

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

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

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

(II-8)

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,  $\coth \frac{2(j+1)\hbar\omega_1^0}{2kT_1}$

$$= (1 + e^{-2(j+1)\hbar\omega_1^0/kT_1}) / (1 - e^{-2(j+1)\hbar\omega_1^0/kT_1})$$

$$\text{and } e^{-j(j+1)\hbar\omega_1^0/kT_1} (1 \pm e^{-2(j+1)\hbar\omega_1^0/kT_1})$$

$$= e^{-j(j+1)\hbar\omega_1^0/kT_1} \pm e^{-(j+1)(j+2)\hbar\omega_1^0/kT_1}$$

The result is



$$\begin{aligned}
\phi_{or}^{(2)} = & -\frac{2\mu_1^2\mu_2^2}{3V_{12}^6\hbar Q_1 Q_2} \left\{ \sum_{j'=0}^{\infty} \left( e^{-j'(j'+1)\hbar\omega_2^0/kT_2} + e^{-(j'+1)(j'+2)\hbar\omega_2^0/kT_2} \right) (j'+1) \right. \\
& \times \sum_{j=0}^{\infty} \left( e^{-j(j+1)\hbar\omega_1^0/kT_1} - e^{-(j+1)(j+2)\hbar\omega_2^0/kT_2} \right) (j+1) \frac{2(j'+1)\omega_1^0}{[2(j'+1)\omega_1^0]^2 - [2(j'+1)\omega_2^0]^2} \\
& - \sum_{j=0}^{\infty} \left( e^{-j(j+1)\hbar\omega_1^0/kT_1} + e^{-(j+1)(j+2)\hbar\omega_1^0/kT_1} \right) (j+1) \\
& \left. \times \sum_{j'=0}^{\infty} \left( e^{-j'(j'+1)\hbar\omega_2^0/kT_2} - e^{-(j'+1)(j'+2)\hbar\omega_2^0/kT_2} \right) (j'+1) \frac{2(j'+1)\omega_2^0}{[2(j'+1)\omega_1^0]^2 - [2(j'+1)\omega_2^0]^2} \right\}
\end{aligned}$$

(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

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

(II-10)

We drop the restriction on the second summation, which has the effect of introducing terms for which  $(j+1)\omega_1^0 = (j'+1)\omega_2^0$  and correct for this effect by subtracting out these singular terms, e.g.

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

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

$$T_{\{1\}} + T_{\{2\}} = \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} e^{-j(j+1)\hbar\omega_1^0/kT_1} e^{-j'(j'+1)\hbar\omega_2^0/kT_2} \times \frac{(j+1)(j'+1)}{2(j+1)\omega_1^0 + 2(j'+1)\omega_2^0} \quad (\text{II-11})$$

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

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

we get

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

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

$$\phi_{or}^{(2)} = -\frac{2\mu_1\mu_2}{3r_{12}^6 \hbar Q_1 Q_2} \left[ \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} (j+1)(j'+1) \right. \\ \left. \times \left\{ \frac{e^{-j(j+1)\hbar\omega_1^0/kT_1} e^{-j'(j'+1)\hbar\omega_2^0/kT_2} - e^{-(j+1)(j+2)\hbar\omega_1^0/kT_1} e^{-(j'+1)(j'+2)\hbar\omega_2^0/kT_2}}{2(j+1)\omega_1^0 + 2(j'+1)\omega_2^0} \right\} \right. \\ \left. + \left\{ \frac{e^{-j(j+1)\hbar\omega_1^0/kT_1} e^{-(j'+1)(j'+2)\hbar\omega_2^0/kT_2} - e^{-(j+1)(j+2)\hbar\omega_1^0/kT_1} e^{-j'(j'+1)\hbar\omega_2^0/kT_2}}{2(j+1)\omega_1^0 - 2(j'+1)\omega_2^0} \right\} \right]$$

(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

$(j+1)\omega_1^0 = (j'+1)\omega_2^0$  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 cotangent 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

$$\begin{aligned} \phi_{\text{or}}^{(2)} &= -\frac{4\mu_1^2\mu_2^2}{3V_{12}^6\hbar} \cdot \frac{1}{\left(\int_0^\infty (2j+1)e^{-j(j+1)\hbar\omega_1^0/kT_1} dj\right)} \cdot \frac{1}{\left(\int_0^\infty (2j'+1)e^{-j'(j'+1)\hbar\omega_2^0/kT_2} dj'\right)} \\ &\times \frac{\hbar}{\omega_1^0 kT_1} \cdot \frac{\hbar}{\omega_2^0 kT_2} \left[ \frac{kT_2}{\hbar} \int_0^\infty dj' \int_0^\infty dj e^{-j(j+1)\hbar\omega_1^0/kT_1} e^{-j'(j'+1)\hbar\omega_2^0/kT_2} \right. \\ &\times \left. \frac{[(j'+1)\omega_1^0]^3 [(j'+1)\omega_2^0]}{[(j'+1)\omega_1^0]^2 - [(j'+1)\omega_2^0]^2} \right. \\ &+ \left. \frac{kT_1}{\hbar} \int_0^\infty dj \int_0^\infty dj' e^{-j(j+1)\hbar\omega_1^0/kT_1} e^{-j'(j'+1)\hbar\omega_2^0/kT_2} \right. \\ &\times \left. \frac{[(j'+1)\omega_2^0]^3 [(j'+1)\omega_1^0]}{[(j'+1)\omega_1^0]^2 - [(j'+1)\omega_2^0]^2} \right] \quad (\text{II-13}) \end{aligned}$$

We next make the substitutions  $(j+1)\omega_1^0 = p$ ,  $(j'+1)\omega_2^0 = q$ ,

$$a = \hbar/\omega_1^0 kT_1 \quad \text{and} \quad b = \hbar/\omega_2^0 kT_2 \quad \text{and replace the}$$

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

$$\begin{aligned} \phi_{\text{or}}^{(2)} = & -\frac{4\mu_1^2\mu_2^2}{3r_{12}^6} \cdot \frac{ab}{kT_1T_2} \left\{ T_2 \int_{\omega_2^0}^{\infty} dq \int_{\omega_1^0}^{\infty} dp e^{-\left(ap^2 - \frac{\hbar p}{kT_1}\right)} e^{-\left(bq^2 - \frac{\hbar q}{kT_2}\right)} \frac{p^3 q}{p^2 - q^2} \right. \\ & \left. + T_1 \int_{\omega_1^0}^{\infty} dp \int_{\omega_2^0}^{\infty} dq e^{-\left(ap^2 - \frac{\hbar p}{kT_1}\right)} e^{-\left(bq^2 - \frac{\hbar q}{kT_2}\right)} \frac{q^3 p}{q^2 - p^2} \right\} \end{aligned}$$

(II-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

$$\begin{aligned} \phi_{\text{or}}^{(2)} = & -\frac{4\mu_1^2\mu_2^2}{3r_{12}^6 kT_1 T_2} \left\{ T_2 \int_{\delta_2}^{\infty} dy \int_{\delta_1}^{\infty} dx e^{-(x^2+y^2)} \frac{x^3 y}{x^2 - \frac{a}{b} y^2} \right. \\ & \left. + T_1 \int_{\delta_1}^{\infty} dx \int_{\delta_2}^{\infty} dy e^{-(x^2+y^2)} \frac{y^3 x}{y^2 - \frac{b}{a} x^2} \right\} \end{aligned}$$

(II-15)

The lower limits of integration  $\delta_1$  and  $\delta_2$  are respectively

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

and

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

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  $dx dy = r dr d\theta$ ) we get for the first double integral

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

$$= -\frac{1}{2} \frac{b}{a+b} \int_0^1 \frac{t^3}{\kappa^2 - t^2} dt \quad (\text{II-16})$$

where  $t = \cos \theta$  and  $\kappa^2 = a/a+b$ . (The factor of  $\frac{1}{2}$  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

$$\int_0^1 = \lim_{\epsilon \rightarrow 0} \left[ \int_0^{\kappa - \epsilon} + \int_{\kappa + \epsilon}^1 \right]$$

presents no special difficulties and yields

$$\int_0^1 \frac{t^3}{\kappa^2 - t^2} dt = - \left[ \frac{1}{2} + \frac{1}{2} \kappa^2 \ln \frac{1 - \kappa^2}{\kappa^2} \right] \quad (\text{II-17})$$

Substitution into (II-16) gives

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

A similar analysis shows that the second double integral of Eq. (II-15) produces

$$B = \int_0^{\infty} dx \int_0^{\infty} dy e^{-(x^2+y^2)} \frac{y^3 x}{y^2 - \frac{b}{a} x^2} \quad (\text{II-19})$$

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

Since

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

and

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

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

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

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

$$\Phi_{\text{or}}^{(2)} = - \frac{\mu_1^2 \mu_2^2}{3k T_1 T_2 r_{12}^6} \left\{ T_2 \frac{f_1}{f_1 + f_2} + T_1 \frac{f_2}{f_1 + f_2} + (T_2 - T_1) \frac{f_1 f_2}{(f_1 + f_2)^2} \ln \frac{f_1}{f_2} \right\} \quad (\text{II-20})$$

We may consider three special cases:

i)  $T_1 = T_2 = T$ . The usual Keesom potential is then recovered<sup>7</sup>:

$$\Phi_{\text{or}}^{(2)} = - \frac{\mu_1^2 \mu_2^2}{3k T r_{12}^6} \quad (\text{II-21})$$

ii)  $f_1 = f_2$  or  $T_1 / I_1 = T_2 / I_2$ . The potential then becomes

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

This potential corresponds to the average potential energy proposed by Schumacher, Bernstein and Rothe<sup>4</sup>.

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

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



### 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

$$\ln \xi^{1/2} = \coth \ln \xi^{1/2} \quad (\text{III-1})$$

where  $\xi$  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  $W_{2 \rightarrow 1}$  and  $W_{1 \rightarrow 2}$  (Eqs. II-2 and II-3) both positive and negative terms occur: the positive terms of, say,  $W_{2 \rightarrow 1}$  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.

$$\begin{aligned} \exp\{-j(j+1)\hbar\omega_i^0/kT_1\} &= \exp\{-E_j^{(1)}/kT_1\} \quad , \\ \exp\{-(j+1)(j+2)\hbar\omega_i^0/kT_1\} &= \exp\{-E_{j+1}^{(1)}/kT_1\} \quad , \\ -2(j+1)\omega_i^0 &= (E_j^{(1)} - E_{j+1}^{(1)})/\hbar \quad , \end{aligned}$$

etc. and make the following substitutions (see Appendix)

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

and

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

we get

$$\begin{aligned}
\phi_{\text{or}}^{(2)} = & -\frac{6}{r_{12}^6 Q_1 Q_2} \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} |e z_{j,j+1}^{(1)}|^2 |e z_{j',j'+1}^{(2)}|^2 \\
& \times \left\{ \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} - e^{-E_{j+1}^{(1)}/kT_1} e^{-E_{j'+1}^{(2)}/kT_2}}{(E_{j+1}^{(1)} + E_{j'+1}^{(2)}) - (E_j^{(1)} + E_{j'}^{(2)})} \right. \\
& \left. + \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{j'+1}^{(2)}/kT_2} - e^{-E_{j+1}^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2}}{(E_{j+1}^{(1)} + E_{j'}^{(2)}) - (E_j^{(1)} + E_{j'+1}^{(2)})} \right\} \quad (\text{III-3})
\end{aligned}$$

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

$$\begin{aligned}
\phi_{\text{or}}^{(2)} = & -\frac{6}{r_{12}^6 Q_1 Q_2} \left\{ \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} \frac{e^{-E_i^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} |e z_{j,j+1}^{(1)}|^2 |e z_{j',j'+1}^{(2)}|^2}{(E_{j+1}^{(1)} + E_{j'+1}^{(2)}) - (E_j^{(1)} + E_{j'}^{(2)})} \right. \\
& + \sum_{i=1}^{\infty} \sum_{i'=1}^{\infty} \frac{e^{-E_i^{(1)}/kT_1} e^{-E_{i'}^{(2)}/kT_2} |e z_{i,i-1}^{(1)}|^2 |e z_{i',i'-1}^{(2)}|^2}{(E_{i-1}^{(1)} + E_{i'-1}^{(2)}) - (E_i^{(1)} + E_{i'}^{(2)})} \\
& + \sum_{j=0}^{\infty} \sum_{i'=1}^{\infty} \frac{e^{-E_j^{(1)}/kT_1} e^{-E_{i'}^{(2)}/kT_2} |e z_{j,j+1}^{(1)}|^2 |e z_{i',i'-1}^{(2)}|^2}{(E_{j+1}^{(1)} + E_{i'-1}^{(2)}) - (E_j^{(1)} + E_{i'}^{(2)})} \\
& \left. + \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \frac{e^{-E_i^{(1)}/kT_1} e^{-E_{j'}^{(2)}/kT_2} |e z_{i,i-1}^{(1)}|^2 |e z_{j',j'+1}^{(2)}|^2}{(E_{i-1}^{(1)} + E_{j'+1}^{(2)}) - (E_i^{(1)} + E_{j'}^{(2)})} \right\} \quad (\text{III-4})
\end{aligned}$$

or, more compactly

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

where  $j$  and  $j'$  run from 0 to  $\infty$  and  $\eta = j \pm 1 \geq 0$  and  $\eta' = j' \pm 1 \geq 0$ . 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<sup>8</sup>, we can replace the quantity

$$(6/r_{12}^6) |e z_{j,\eta}^{(1)}|^2 |e z_{j',\eta'}^{(2)}|^2$$

by

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

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

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

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

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

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.

Appendix: Frequency-Dependent Susceptibility of a Rotating Dipole

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  $\omega$ . The imaginary part of the response function can be derived by application of the formal expression<sup>9</sup>

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

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 wavefunction 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

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

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

(A-3)

= 0

otherwise.

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

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

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

(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.

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

we can write

$$\beta''(\omega) = \frac{\pi(1 - e^{-\hbar\omega/kT})}{\hbar Q} \left\{ \sum_{j=0}^{\infty} e^{-E_j/kT} \sum_{m=-j}^j |e z_{j,m;j+1,m}|^2 \delta(\omega + \omega_{j,j+1}^{\circ}) \right. \\ \left. + \sum_{j=1}^{\infty} e^{-E_j/kT} \sum_{m=-j}^j |e z_{j,m;j-1,m}|^2 \delta(\omega + \omega_{j,j-1}^{\circ}) \right\} \quad (\text{A-5})$$

where

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

and

$$\omega_{j,j-1}^{\circ} = 2j\omega^{\circ} .$$

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

$$\sum_{m=-j}^j |e z_{j,m;j+1,m}|^2 = e^2 v_0^2 \sum_{m=-j}^j \frac{(j+1)^2 - m^2}{(2j+3)(2j+1)} \\ = \mu^2 \left\{ \frac{(j+1)^2(2j+1) - \frac{1}{3}(2j+1)j(j+1)}{(2j+3)(2j+1)} \right\} \\ = \frac{1}{3} \mu^2 (j+1) \quad (\text{A-6})$$



$$\begin{aligned}
 \text{and} \\
 \sum_{m=-j}^j |e z_{j,m;j-1,m}|^2 &= e^2 r_0^2 \sum_{m=-j}^j \frac{j^2 - m^2}{(2j+1)(2j-1)} \\
 &= \mu^2 \left\{ \frac{j^2(2j+1) - \frac{1}{3}(2j+1)j(j+1)}{(2j+1)(2j-1)} \right\} \\
 &= \frac{1}{3} \mu^2 j
 \end{aligned} \tag{A-7}$$

where use has been made of the relation<sup>8</sup>

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

Substitution of (A-6) and (A-7) into (A-5), gives the final result

(see also comments in footnote ref. 6):

$$\begin{aligned}
 \beta''(\omega) &= \frac{\pi \mu^2 (1 - e^{-\hbar\omega/kT})}{3\hbar Q} \left\{ \sum_{j=0}^{\infty} e^{-j(j+1)\hbar\omega/kT} (j+1) \delta(\omega + \omega_{j,j+1}^0) \right. \\
 &\quad \left. + \sum_{j=1}^{\infty} e^{-j(j+1)\hbar\omega/kT} j \delta(\omega + \omega_{j,j-1}^0) \right\}
 \end{aligned} \tag{A-8}$$

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

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \int_0^\infty dy \frac{y}{y^2 - \omega^2} (1 - e^{-\hbar y/kT}) \sum_{j=0}^\infty e^{-j(j+1)\hbar\omega^0/kT} (j+1) \delta(y + \omega_{j,j+1}^0) \quad (\text{A-9})$$

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

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \sum_{j=0}^\infty \frac{2(j+1)^2 \omega^0 (1 - e^{-2(j+1)\hbar\omega^0/kT}) e^{-j(j+1)\hbar\omega^0/kT}}{[2(j+1)\omega^0]^2 - \omega^2} \quad (\text{A-10})$$

or

$$\beta'(\omega) = \frac{2\mu^2}{3\hbar Q} \sum_{j=0}^\infty \frac{2(j+1)^2 \omega^0 (e^{-j(j+1)\hbar\omega^0/kT} - e^{-(j+1)(j+2)\hbar\omega^0/kT})}{[2(j+1)\omega^0]^2 - \omega^2} \quad (\text{A-11})$$

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

$$\beta'(0) = \beta(0) = \frac{2\mu^2}{3\hbar Q} \cdot \frac{1}{2\omega^0} = \frac{\mu^2}{3\hbar\omega^0 \sum_{j=0}^\infty (2j+1) e^{-j(j+1)\hbar\omega^0/kT}} \quad (\text{A-12})$$

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 22, 129 (1921).
2. R. H. Cole, J. Chem. Phys. 39, 2602 (1963).
3. E. W. Rothe and R. B. Bernstein, J. Chem. Phys. 31, 1619 (1959).
4. H. Schumacher, R. B. Bernstein and E. W. Rothe, J. Chem. Phys. 33, 584 (1960).
5. B. Linder, J. Chem. Phys. 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.

### Acknowledgement

Grateful acknowledgement is made to Prof. R. B. Bernstein, not only for his initial suggestion of this problem but also for his continued interest and encouragement during the author's stay at the University of Wisconsin. I also wish to thank Prof. J. O. Hirschfelder, director of the Theoretical Chemistry Institute of the University of Wisconsin and Prof. J. de Boer, director of the Institute of Theoretical Physics of the University of Amsterdam for their hospitality and interest in this work. I am indebted to Drs. J. Groeneveld for checking some of the results and to Mrs. A. Mansvelt Beck and Mrs. M. Wilson for typing the manuscript.

This research has received direct and indirect support from the following sources: The Petroleum Research Fund administered by the American Chemical Society, the National Aeronautic and Space Administration and the Guggenheim Foundation. Grateful acknowledgement is made to the donors of said funds.

#### Footnote 1:

This research was initiated, on a suggestion by Prof. R. B. Bernstein, at the Theoretical Chemistry Institute of the University of Wisconsin where the author spent the summer of 1964, and completed at the Institute of Theoretical Physics of the University of Amsterdam during the author's tenure under a Guggenheim Fellowship, year 1964-1965.