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Asymptotic evaluation of the Keesom integral

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Abstract
A simple physically transparent formula is obtained in the asymptotic evaluation of the Keesom integral $K(a)$ for large values of the parameter a. Its derivation is described in some detail and the asymptotic formula is compared with the results obtained from direct three-dimensional numerical integration.

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1. Introduction

In 1921 Keesom [1] pointed out that if two molecules possessing a permanent dipole moment undergo thermal motions, they will on average assume orientations leading to attraction.

If $(\theta_A, \theta_B, \varphi) = \Omega$ are the angles describing the mutual orientation of dipoles of strength μ_A and μ_B, the interaction between the dipoles at distance R between their centres is given by [2]

$$V(\Omega, R) = \frac{\mu_A \mu_B}{R^3} F(\Omega) \tag{1}$$

$$F(\Omega) = \sin\theta_A \sin\theta_B \cos\varphi - 2\cos\theta_A \cos\theta_B. \tag{2}$$

The Boltzmann probability for a dipole arrangement having energy V is proportional to

$$W \propto \exp(-V/kT) \tag{3}$$

where k is the Boltzmann constant. Averaging the quantity $V \exp(-V/kT)$ over the domain S of all possible orientations Ω assumed by the dipoles gives

$$\langle V \exp(-V/kT)\rangle = \frac{\mu_A \mu_B}{R^3} \frac{\int_S \mathrm{d}\Omega\, F(\Omega) \exp[aF(\Omega)]}{\int_S \mathrm{d}\Omega \exp[aF(\Omega)]} = \frac{\mu_A \mu_B}{R^3} \frac{\mathrm{d}}{\mathrm{d}a} \ln K(a) \tag{4}$$

where

$$a = -\frac{\mu_A \mu_B}{R^3 kT} \tag{5}$$

is a dimensionless parameter depending on R, T, and on the strength of the dipoles, and

$$K(a) = \int_S \mathrm{d}\Omega \exp[aF(\Omega)] \tag{6}$$

is called the Keesom integral.

The aim of this paper is the analytic evaluation of $K(a)$ for large values of the parameter a. An asymptotic series expansion in inverse powers of $(-a)$ is obtained for the logarithmic derivative, whose first three terms describe in a physically transparent way the temperature dependence of the interaction energy for low values of T.

2. The complete asymptotic series

Changing variables from θ_A, θ_B to α, β defined as

$$\alpha = \theta_A + \theta_B, \qquad \beta = \theta_B - \theta_A, \tag{7}$$

we note that the integral $K(a)$ is perfectly well defined by equation (6), with the domain S of integration defined by

$$0 \leqslant \theta_A, \theta_B \leqslant \pi, \qquad -\frac{\pi}{2} \leqslant \varphi \leqslant \frac{3\pi}{2}$$

or, because of symmetrization, restricting the variable range to

$$-\frac{\pi}{2} \leqslant \varphi \leqslant \frac{\pi}{2}$$

and by multiplying the result by 2. At point $\varphi = 0$ the integrand of (6) has no poles so that the path of integration may be shifted into the complex plane over a half-circle surrounding the point $\varphi = 0$ without changing the value of the integral [3]. This may be subsequently evaluated by integration by parts along this path, so avoiding the singularities, the result being of course the same as that of the original integral. Hence the Keesom integral (6) can be transformed into

$$\begin{aligned} K(a) &= -\frac{2}{a} \int_{-\pi/2}^{(3\pi)/2} \frac{\mathrm{d}\varphi}{\sin\varphi} \frac{\partial}{\partial\varphi} \left[\int_0^\pi \mathrm{d}\alpha \int_0^\alpha \mathrm{d}\beta \exp[aF(\Omega)] \right] \\ &= \left(-\frac{2}{a} \frac{1}{\sin\varphi} \right) \int_0^\pi \mathrm{d}\alpha \int_0^\alpha \mathrm{d}\beta \exp[aF(\Omega)] \Bigg|_{\varphi=-\frac{\pi}{2}}^{\varphi=\frac{3\pi}{2}} \\ &\quad - \int_{-\pi/2}^{(3\pi)/2} \mathrm{d}\varphi \left[\int_0^\pi \mathrm{d}\alpha \int_0^\alpha \mathrm{d}\beta \exp[aF(\Omega)] \right] \frac{\mathrm{d}}{\mathrm{d}\varphi} \left[-\frac{2}{a} \frac{1}{\sin\varphi} \right] \\ &= -\frac{2}{a} \int_{-\pi/2}^{(3\pi)/2} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \int_0^\pi \mathrm{d}\alpha \int_0^\alpha \mathrm{d}\beta \exp[aF(\Omega)] \end{aligned} \tag{8}$$

where the finite factor vanishes in the limit because of periodicity. The integration range over α and β is restricted to the grey region in figure 1 taking into account the symmetries of $F(\Omega)$.

We now expand the exponential into the infinite series,

$$\exp[aF(\Omega)] = \mathrm{e}^{-2a} \exp\left\{ \frac{a}{2}\rho^2 \left(1 + \frac{1}{2}\cos 2\eta \cos\varphi \right) \right\} \sum_{\lambda=0}^{\infty} \frac{(-a)^\lambda}{\lambda!} \left[\sum_{n=2}^{\infty} \frac{(-1)^n}{(2n)!} \rho^{2n} f_{2n}(\eta, \varphi) \right]^\lambda \tag{9}$$

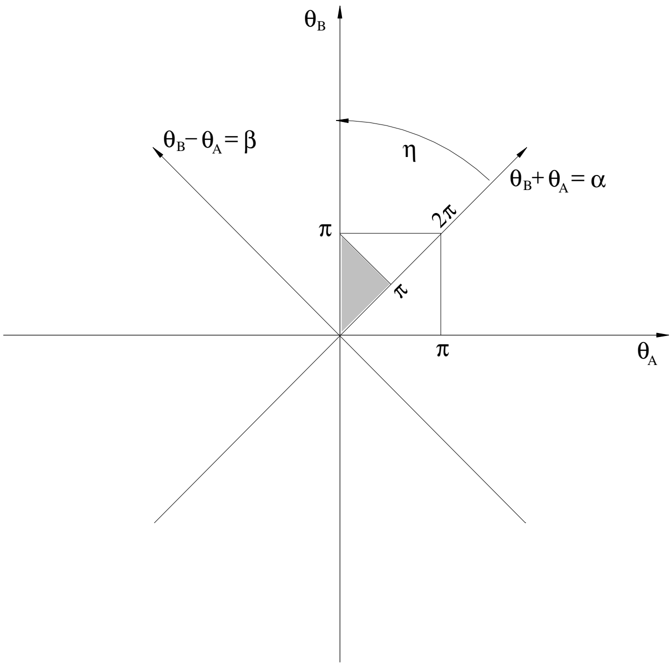

Figure 1. Illustration of variable transformation and integration range. The exact integration range is represented by the grey area.

where

$$f_{2n}(\eta,\varphi) = [(\cos\eta)^{2n} + (\sin\eta)^{2n}] + \frac{1}{2}\cos\varphi[(\cos\eta)^{2n} - (\sin\eta)^{2n}]$$

$$(\cos\eta)^{2n} \pm (\sin\eta)^{2n} = \frac{1}{2^n}[(1+\cos 2\eta)^n \pm (1-\cos 2\eta)^n], \tag{10}$$

$$\rho^2 = \alpha^2 + \beta^2, \qquad \eta = \tan^{-1}\frac{\beta}{\alpha}.$$

In the integration, ρ must go from 0 to the straight line which is the skew diagonal of the square, satisfying $\rho\cos\eta = \pi$ (figure 1). Hence, the upper extremum of integration over $\mathrm{d}\rho^2$ may appropriately be written as

$$X = (-a)\rho^2 = (-a)\frac{\pi^2}{\cos^2\eta} \tag{11}$$

and, changing variable to

$$(-a)\rho^2 = x \qquad \mathrm{d}\rho^2 = \frac{\mathrm{d}x}{(-a)} \tag{12}$$

we get the Keesom integral in the form

$$K(a) = -\frac{\exp(-2a)}{a}\int_{-\pi/2}^{(3\pi)/2}\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\int_0^{\pi/4}\mathrm{d}\eta\int_0^X \mathrm{d}x\exp\left\{-\frac{1}{2}x\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)\right\}$$
$$\times\sum_{\lambda=0}^{\infty}\frac{1}{\lambda!}\sum_{n_1=2}^{\infty}\sum_{n_2=2}^{\infty}\cdots\sum_{n_\lambda=2}^{\infty}\frac{(-1)^{n_1+n_2+\cdots+n_\lambda}}{(2n_1)!(2n_2)!\cdots(2n_\lambda)!}\frac{x^{n_1+n_2+\cdots+n_\lambda}f_{2n_1}f_{2n_2}\cdots f_{2n_\lambda}}{(-a)^{n_1+n_2+\cdots+n_\lambda+1-\lambda}}. \tag{13}$$

Carrying the integration over dx, putting

$$n_1 + n_2 + \cdots + n_\lambda + 1 - \lambda = \kappa \tag{14}$$

and collecting all terms with the same value of κ, we obtain

$$\begin{aligned} K(a) = &-\frac{\exp(-2a)}{a}\int_{-\pi/2}^{(3\pi)/2} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi}\int_0^{\pi/4}\mathrm{d}\eta \sum_{\kappa=1}^{\infty}\frac{1}{(-a)^\kappa}\sum_{\lambda=0}^{\kappa-1}\frac{1}{\lambda!} \\ &\times \sum_{n_1=2}^{\infty}\sum_{n_2=2}^{\infty}\cdots\sum_{n_\lambda=2}^{\infty}\frac{f_{2n_1}(\eta,\varphi)f_{2n_2}(\eta,\varphi)\cdots f_{2n_\lambda}(\eta,\varphi)}{(2n_1)!(2n_2)!\cdots(2n_\lambda)!}\left[\frac{(-1)^{\kappa+\lambda-1}2^{\kappa+\lambda}(\kappa+\lambda-1)!}{\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)^{\kappa+\lambda}}\right. \\ &\left. + (-1)^{\kappa+\lambda}\exp\left\{-\frac{1}{2}(-a)\frac{\pi^2}{\cos^2\varphi}\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)\right\}\frac{2\left[(-a)\frac{\pi^2}{\cos^2\eta}\right]^{\kappa+\lambda-1}}{1+\frac{1}{2}\cos 2\eta\cos\varphi} + \text{h.o.t.}\right]. \end{aligned} \tag{15}$$

By neglecting the last terms which are exponentially small, we obtain the *complete* expansion of $K_\infty(a)$ in inverse powers of $(-a)$:

$$\begin{aligned} K_\infty(a) \cong &-\frac{\exp(-2a)}{a}\sum_{\kappa=1}^{\infty}\frac{1}{(-a)^\kappa}\sum_{\lambda=0}^{\kappa-1}\frac{(-1)^{\kappa+\lambda-1}2^{\kappa+\lambda}(\kappa+\lambda-1)!}{\lambda!} \\ &\times \sum_{n_1\geqslant 2}\sum_{n_2\geqslant 2}\cdots\sum_{n_\lambda\geqslant 2}\frac{1}{(2n_1)!(2n_2)!\cdots(2n_\lambda)!} \\ &\times \int_{-\pi/2}^{(3\pi)/2}\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\int_0^{\pi/4}\mathrm{d}\eta\frac{f_{2n_1}(\eta,\varphi)f_{2n_2}(\eta,\varphi)\cdots f_{2n_\lambda}(\eta,\varphi)}{\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)^{\kappa+\lambda}}. \end{aligned} \tag{16}$$

The λ-fold sum over integers n_j $(j = 2, 3, \ldots, \lambda)$ is constrained by condition (14). The maximum value of n_j is obtained by setting all the remaining n_i $(i \neq j)$ equal to their minimum value, which yields

$$n_j = \kappa - \lambda + 1. \tag{17}$$

We obtain in this way an infinite series expansion in $(-a)^{-\kappa}$ with numerical coefficients which are the sum of a finite number of terms, which can be calculated either analytically or numerically.

3. Evaluation of the leading terms of the resulting integral

We now take into explicit consideration the first two terms $\kappa = 1, 2$ in the asymptotic evaluation of the integral (13). The approximate form of the integrand allows us to get rid of the upper extremum of integration over dα with little error (see equation (15)):

$$\begin{aligned} \exp[aF(\Omega)] &= \exp\left\{-a\left[\left(1-\frac{1}{2}\cos\varphi\right)\cos\beta + \left(1+\frac{1}{2}\cos\varphi\right)\cos\alpha\right]\right\} \\ &\cong \exp(-2a)\exp\left\{\frac{a}{2}\,(\alpha^2+\beta^2) + \frac{a}{4}(\alpha^2-\beta^2)\cos\varphi \right. \\ &\quad \left. - \frac{a}{4!}(\alpha^4+\beta^4)\; - \frac{1}{2}\frac{a}{4!}(\alpha^4-\beta^4)\cos\varphi\right\} \\ &\cong \exp(-2a)\exp\left\{\frac{a}{2}(\alpha^2+\beta^2) + \frac{a}{4}(\alpha^2-\beta^2)\cos\varphi\right\} \\ &\quad \times\left[1 - \frac{a}{4!}\left((\alpha^4+\beta^4) + \frac{1}{2}(\alpha^4-\beta^4)\cos\varphi\right)\right]. \end{aligned} \tag{18}$$

The asymptotic formula is obtained by pushing to infinity the upper extremum of integration over $\mathrm{d}\alpha$:

$$K_\infty(a) \cong -\frac{\exp(-2a)}{a} \int_{-\pi/2}^{(3\pi)/2} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \int_0^{\pi/4} \mathrm{d}\eta \int_0^{\infty} \mathrm{d}\rho^2 \exp\left\{\frac{a}{2}\rho^2\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)\right\} \times \left\{1 - \frac{1}{2}\frac{a}{4!}\rho^4(1+\cos^2 2\eta + \cos 2\eta\cos\varphi)\right\}. \tag{19}$$

Performing the integration over $\mathrm{d}\rho^2$ we obtain

$$K_\infty(a) \cong -\frac{\exp(-2a)}{a^2} \int_{-\pi/2}^{(3\pi)/2} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \int_0^{\pi/4} \mathrm{d}\eta \times \left\{\frac{-2}{1+\frac{1}{2}\cos 2\eta\cos\varphi} + \frac{1+\cos^2 2\eta + \cos 2\eta\cos\varphi}{3a\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)^3}\right\}. \tag{20}$$

Symmetrization of the integrand $f(\cos\varphi)$ gives

$$\frac{f(\cos\varphi)+f(-\cos\varphi)}{2} = \frac{\cos^2\varphi}{\sin^2\varphi}\int_0^{\pi/4} \mathrm{d}\eta\cos 2\eta \left\{\frac{1}{1-\frac{1}{4}\cos^2 2\eta\cos^2\varphi} - \frac{\frac{1}{2}+\frac{3}{2}\cos^2 2\eta - \frac{5}{8}\cos^2 2\eta\cos^2\varphi + \frac{1}{8}\cos^4 2\eta\cos^2\varphi}{3a\left(1-\frac{1}{4}\cos^2 2\eta\cos^2\varphi\right)^3}\right\}. \tag{21}$$

Since (21) to be integrated over φ has singularities at points $\varphi = \pm n\pi$ with integer n, these points must be bypassed by shifting the path of integration into the complex plane, as explained above. By changing to variables $\psi = 2\eta$ and $y = \tan\varphi$, putting $b^2 = 1 - \frac{1}{4}\cos^2\psi$, we obtain

$$K_\infty(a) \cong \frac{\exp(-2a)}{a^2}\int_0^{\pi/2} \mathrm{d}\psi\cos\psi \int_{-\infty}^{+\infty} \mathrm{d}y \times \left\{\frac{-1}{y^2(y^2+b^2)} + \frac{\frac{1}{2}(1+3\cos^2\psi)(1+y^2)^2}{3ay^2(y^2+b^2)^3} - \frac{\frac{1}{8}(5\cos^2\psi - \cos^4\psi)(1+y^2)}{3ay^2(y^2+b^2)^3}\right\}. \tag{22}$$

The integrals above are evaluated by decomposing the rational functions of y^2 into their multiple-pole expansion according to the identities,

$$\frac{1}{y^2(y^2+b^2)} = \frac{1}{b^2}\left(\frac{1}{y^2} - \frac{1}{y^2+b^2}\right) \tag{23}$$

$$\frac{(1+y^2)^2}{y^2(y^2+b^2)^3} = \frac{1}{b^6}\frac{1}{y^2} - \frac{(1-b^2)^2}{b^2}\frac{1}{(y^2+b^2)^3} + \frac{b^4-1}{b^4}\frac{1}{(y^2+b^2)^2} - \frac{1}{b^6}\frac{1}{y^2+b^2} \tag{24}$$

$$\frac{1+y^2}{y^2(y^2+b^2)^3} = \frac{1}{b^6}\frac{1}{y^2} - \frac{1-b^2}{b^2}\frac{1}{(y^2+b^2)^3} - \frac{1}{b^4}\frac{1}{(y^2+b^2)^2} - \frac{1}{b^6}\frac{1}{y^2+b^2} \tag{25}$$

then using the formula resulting from integration in the complex plane [4]:

$$\int_{-\infty}^{+\infty} \frac{\mathrm{d}y}{(y^2+b^2)^n} = \frac{(2n-3)!!}{(2n-2)!!}\frac{\pi}{b^{2n-1}}. \tag{26}$$

A simple calculation gives

$$K_\infty(a) = \pi\frac{\exp(-2a)}{a^2}\int_0^{\pi/2} \mathrm{d}\psi\cos\psi\left\{\frac{1}{\left(1-\frac{1}{4}\cos^2\psi\right)^{3/2}} - \frac{\cos^4\psi + \frac{11}{8}\cos^2\psi + 1}{6a\left(1-\frac{1}{4}\cos^2\psi\right)^{7/2}}\right\}. \tag{27}$$

Table 1. Logarithmic derivative of the Keesom integral $K_\infty(a)$ for large values of the parameter a to order a^{-2}.

$-a$	Asymptotic	Correct	|Error|	$2/(3a^2)$
5	−1.573 333	−1.544 076	0.029 257	0.026 667
10	−1.793 333	−1.790 538	0.002 795	0.006 667
15	−1.863 704	−1.863 068	0.000 636	0.002 963
20	−1.898 333	−1.898 091	0.000 242	0.001 667
30	−1.932 593	−1.932 527	0.000 066	0.000 741
40	−1.949 583	−1.949 556	0.000 027	0.000 417
50	−1.959 733	−1.959 720	0.000 013	0.000 267
100	−1.979 933	−1.979 932	0.000 001	0.000 067

Turning to hyperbolic functions, the further substitutions,

$$\begin{aligned} &\sin\psi = \sqrt{3}\sinh t && \mathrm{d}\sin\psi = \sqrt{3}\cosh^3 t\,\mathrm{d}\tanh t \\ &\tanh t = x && \tanh\left(\sinh^{-1}\tfrac{1}{\sqrt{3}}\right) = \tfrac{1}{2} \end{aligned} \tag{28}$$

reduce the last integral to the elementary form

$$\int_0^{1/2} \mathrm{d}x \left\{\frac{8}{3} - \frac{8}{9a}(3 - 15x^2 + 20x^4)\right\} = \frac{4}{3} - \frac{8}{9a} \tag{29}$$

giving as our final expression for the asymptotic evaluation of the Keesom integral (6) the simple result:

$$K_\infty(a) \cong \frac{4\pi}{3}\frac{\exp(-2a)}{a^2}\left(1 - \frac{2}{3a}\right). \tag{30}$$

4. Comparison with the results of numerical integration and physical interpretation of the results

Comparison with the results of three-dimensional numerical integration run on Mathematica 2.2® [5] is best done in terms of the logarithmic derivative of the Keesom integral (30):

$$\frac{\mathrm{d}\ln K_\infty(a)}{\mathrm{d}a} \cong -2 - \frac{2}{a} + \frac{2}{3a^2}\left(1 - \frac{2}{3a}\right)^{-1} \cong -2 - \frac{2}{a} + \frac{2}{3a^2} \quad \text{to order } a^{-2}. \tag{31}$$

The results to six decimal digits are given in table 1. To this accuracy there is complete equivalence between the results of numerical integration and those of the full series expansion where terms are added until complete convergence is reached within a predetermined threshold. We shall refer to the latter as Correct. The asymptotic approximation monotonically overestimates the correct value by a quantity which rapidly decreases with increasing the value of the parameter a. Three decimal figures agreement is reached already at $a = -15$. In the third column the absolute values of the error, defined as

$$|\text{Error}| = |\text{Asymptotic}| - |\text{Correct}| \tag{32}$$

are compared with the term $\frac{2}{3a^2}$. It is observed that $|\text{Error}| < \frac{2}{3a^2}$ from $a = -10$ onwards, while for $a = -5$ the situation is reversed. This means that for small values of a the asymptotic expansion diverges. According to Laurentiev and Chabat [3] and Erdèlyi [6] a power series is said to be asymptotically convergent if the error which results from replacing the function $S(z)$ of the complex variable z by a partial sum $S_n(z)$ of the same series is infinitesimal of a order higher than the last term of the partial sum when $z \to \infty$. It is seen that for $z = -a$ this condition is clearly fulfilled by the numbers given in the last two columns of table 1, so that, at least in the range of values given in the table, the expansion is asymptotically convergent.

The simple result of equation (31), introduced in equation (4), gives the first three terms of the expansion of $\langle V \exp(-V/kT)\rangle$ in powers of T for low values of the temperature and has a transparent physical interpretation. This matter is further discussed to some extent in the appendix. The first term, independent of T, gives the zero-point attraction of the dipoles at their minimum energy position, the head-to-tail linear configuration (see also [7, 8]). The second term, proportional to T, gives the mean potential energy of a couple of bidimensional oscillators of different force constants described by the variables α and β, with an entropic factor $(\alpha^2 - \beta^2)$ which vanishes in the equilibrium position ($\alpha = \beta = 0$) [9]. The third term, proportional to T^2, corresponds to the non-quadratic part of the potential.

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Appendix. Small fluctuations around the dipole equilibrium positions

In a first approximation we have two independent linear oscillators for each dipole, which undergo small oscillations around their equilibrium head-to-tail positions inside each one of two arbitrary orthogonal planes that intersect through a straight line connecting the two dipoles. We denote the small angular deviations of each oscillator in the corresponding plane as $\theta_A^{(\xi)}, \theta_A^{(\eta)}$ for dipole A, and $\theta_B^{(\xi)}, \theta_B^{(\eta)}$ for dipole B, where ξ, η are orthogonal coordinate axes in each of the two planes pointing in a direction orthogonal to the straight line joining the dipoles, which we call the ζ-axis. Then

$$\theta_A = \sqrt{\theta_A^{(\xi)2} + \theta_A^{(\eta)2}}, \qquad \theta_B = \sqrt{\theta_B^{(\xi)2} + \theta_B^{(\eta)2}} \tag{33}$$

and the potential energy of interaction between the two couples of linear oscillators is, to a quadratic approximation,

$$\begin{aligned} V(\Omega, R) &= \frac{\mu_A \mu_B}{R^3}\left(\theta_A\theta_B\cos\varphi + \theta_A^2 + \theta_B^2 - 2\right) \\ &= \frac{\mu_A \mu_B}{R^3}\left(\theta_A^{(\xi)}\theta_B^{(\xi)} + \theta_A^{(\eta)}\theta_B^{(\eta)} + \theta_A^{(\xi)2} + \theta_A^{(\eta)2} + \theta_B^{(\xi)2} + \theta_B^{(\eta)2} - 2\right). \end{aligned} \tag{34}$$

The Keesom integral (6) is written as the sum-over-states,

$$\begin{aligned} K(a) &\cong \int_{-\infty}^{\infty} \mathrm{d}\theta_A^{(\xi)} \int_{-\infty}^{\infty} \mathrm{d}\theta_A^{(\eta)} \int_{-\infty}^{\infty} \mathrm{d}\theta_B^{(\xi)} \int_{-\infty}^{\infty} \mathrm{d}\theta_B^{(\eta)} \exp\left[aF\left(\theta_A^{(\xi)}, \theta_A^{(\eta)}, \theta_B^{(\xi)}, \theta_B^{(\eta)}\right)\right] \\ &= \int_0^{\infty} \theta_A\,\mathrm{d}\theta_A \int_0^{\infty} \theta_B\,\mathrm{d}\theta_B \int_0^{2\pi} \mathrm{d}\eta_A \int_0^{2\pi} \mathrm{d}\eta_B \exp[aF(\Omega)] \\ &= \frac{1}{2}\int_0^{4\pi} \mathrm{d}\Phi \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\infty} \theta_A\,\mathrm{d}\theta_A \int_0^{\infty} \theta_B\,\mathrm{d}\theta_B \exp[aF(\Omega)] \end{aligned} \tag{35}$$

where

$$\begin{aligned} \eta_A &= \tan^{-1}\frac{\theta_A^{(\eta)}}{\theta_A^{(\xi)}}, \qquad & \eta_B &= \tan^{-1}\frac{\theta_B^{(\eta)}}{\theta_B^{(\xi)}} \\ \varphi &= \eta_B - \eta_A, \qquad & \Phi &= \eta_B + \eta_A. \end{aligned} \tag{36}$$

Here φ is defined as the angle between the directions of the vectors $\left(\theta_A^{(\xi)}, \theta_A^{(\eta)}\right)$ and $\left(\theta_B^{(\xi)}, \theta_B^{(\eta)}\right)$. The last row of equation (35) follows from the symmetries of $F(\Omega)$ and the fact that $\cos(2\pi - \varphi) = \cos\varphi$. The potential energy of interaction is independent of Φ so that it can be dropped from the integration, since it only supplies a constant factor which is cancelled by normalization. Consequently, by using normal coordinates in equation (34), we obtain the average potential energy of four independent linear oscillators as $2kT$, the same result that is obtained from the logarithmic derivative of the linearized Keesom integral.

As far as the non-quadratic part of the potential is concerned, we remark that the full configuration space of the system of two coupled dipoles is the square in figure 1, times the φ dimension (we do not consider the Φ dimension, for rotational symmetry as a whole). This space is endowed with the evident symmetry of the potential energy about the skew diagonal of the square, so that there is another stable equilibrium point ($\alpha = 2\pi$, $\beta = 0$). The direct diagonal of the square is the most probable path for the dipole flopping transition, with an activation energy $\Delta V = -akT$ and $\varphi = \pi$, which corresponds to antiparallel dipoles at the saddle point (but $\Delta V = -3akT$ for $\varphi = 0$). The relaxation times and the quantum tunnelling times for these processes have been studied by us in [10–12]. Our asymptotic series, equation (16), neglects these effects, being constructed so as to take into account only the confinement into the grey region and the symmetrical counterpart with β negative in figure 1. The density accounted for by any finite sum of terms in equation (13) is infinitesimal at least as $\exp\left[\left(\frac{\pi^2}{4} - 2\right)a\right]$ on the piece of skew diagonal which is the border line of the grey region, to be compared with the value $\exp[-a] = \exp[aF(\alpha = \pi, \beta = 0, \varphi = \pi)]$ which results from equation (18).

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