Asymptotic expansion for the Keesom integral

2005 J. Phys. A: Math. Gen. 38 6715

(http://iopscience.iop.org/0305-4470/38/30/007)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **38** (2005) 6715–6728 doi:10.1088/0305-4470/38/30/007

Asymptotic expansion for the Keesom integral

Michele Battezzati[1] **and Valerio Magnasco**[2]

[1] Istituto di Cosmogeofisica del CNR, Corso Fiume 4, 10133 Torino, Italy
[2] Dipartimento di Chimica e Chimica Industriale dell'Università, Via Dodecaneso 31, 16146 Genova, Italy

Received 11 April 2005, in final form 1 June 2005
Published 13 July 2005
Online at stacks.iop.org/JPhysA/38/6715

Abstract
It is proved that the asymptotic series for the leading term $K_\infty(a)$ of the Keesom integral $K(a)$ obtained by us in a previous paper (2004 *J. Phys. A: Math. Gen.* **37** 9677), in order to evaluate $K(a)$ for large values of the interaction parameter a, is indeed an asymptotic expansion of $K(a)$ itself.

PACS number: 31.15.−p

1. Introduction

In a previous paper [1], in the following referred to as I, we have derived an asymptotic series approximating the Keesom integral

$$K(a) = \int_S \mathrm{d}\Omega\, \exp[a\,F(\Omega)], \tag{1}$$

when the dimensionless negative parameter a tends to $-\infty$.

In equation (1), Ω stands for the three angles $(\theta_A, \theta_B, \varphi)$ defining the relative spatial orientation for two dipoles and S is the domain of all possible values assumed by Ω, $F(\Omega)$ being given by

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

while

$$\mathrm{d}\Omega = \sin\theta_A \sin\theta_B\, \mathrm{d}\theta_A\, \mathrm{d}\theta_B\, \mathrm{d}\varphi \tag{2$'$}$$

and the domain of variation is

$$\begin{cases} 0 \leqslant \theta_A, \theta_B \leqslant \pi, \\ -\frac{\pi}{2} \leqslant \varphi \leqslant \frac{3\pi}{2}. \end{cases} \tag{2$''$}$$

The asymptotic series we have derived for the leading term $K_\infty(a)$ of (1), is given by equation (16) of I, whose nth partial sum can be written as

$$K_\infty^{(n)}(a) = -\frac{\exp\{-2a\}}{a}\sum_{\kappa=1}^{n}\frac{1}{(-a)^\kappa}\sum_{\lambda=0}^{\kappa-1}\frac{(-1)^{\kappa+\lambda-1}2^{\kappa+\lambda}(\kappa+\lambda-1)!}{\lambda!}$$
$$\times\sum_{n_1=2}^{\infty}\sum_{n_2=2}^{\infty}\cdots\sum_{n_\lambda=2}^{\infty}\frac{1}{(2n_1)!(2n_2)!\cdots(2n_\lambda)!}\delta_{n_1+n_2+\cdots+n_\lambda,\kappa+\lambda-1}$$
$$\times\int_{-\pi/2}^{(3\pi)/2}\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\int_0^{\pi/4}\mathrm{d}\eta\frac{f_{2n_1}(\eta,\varphi)f_{2n_2}(\eta,\varphi)\cdots f_{2n_\lambda}(\eta,\varphi)}{\left(1+\frac{1}{2}\cos 2\eta\cos\varphi\right)^{\kappa+\lambda}}, \quad (3)$$

where $f_{2n_j}(\eta,\varphi)$, $1 \leqslant j \leqslant \lambda$, are defined in I, and we assume $K_\infty^{(0)} = 0$. The leading term $K_\infty(a)$ is defined as the asymptotic sum of the series given by equation (16) of I, which can be proved to exist for every asymptotic sequence (see [2]). Paper I was mainly devoted to obtain from naïve analytical expressions accurate numerical results in order to prove the asymptotic convergence of the partial sums, and was therefore lacking a detailed proof that the formal series which was given there by equation (16) is actually convergent, in a proper sense, to $K(a)$.

The aim of this paper is to prove that the partial sum (3) is an *asymptotic expansion*, in the sense defined by Erdèlyi [2], of the Keesom integral $K(a)$. The proof proceeds by splitting the domain of integration over the azimuthal angles into two subintervals, in the first of which the partially expanded exponential weight function converges uniformly, and gives the major contribution to the integral, while in the second one the contribution is exponentially small.

The integral over the cyclic angle φ is bounded by choosing a suitable path of integration inside the complex plane, which avoids the poles of order 2 at

$$\varphi = 0, \pm n\pi$$

with n integer. A further condition is that it should not enclose the poles at the points that satisfy

$$\begin{cases}\mathrm{Re}(\cos\varphi) = -\frac{2}{\cos\eta},\\ \mathrm{Im}(\cos\varphi) = 0,\end{cases} \qquad \text{with} \qquad \begin{cases}\mathrm{Re} = \text{real part},\\ \mathrm{Im} = \text{imaginary part},\end{cases}$$

in the closed region whose boundaries are the integration path and the real axis. This condition is fulfilled by requiring (see section 4)

$$|\mathrm{Re}(\cos\varphi)| < 2.$$

2. Statement of the problem

It should be noted that the partial sum (3) diverges when $n \to \infty$, because, if summed according to Borel, it yields the integral between 0 and ∞ of a periodic positive definite function. On the other hand, we shall prove that

$$\left|\Delta K_\infty^{(n)}(a)\right| = \left|K(a) - K_\infty^{(n)}(a)\right| = o\left(\left|K_\infty^{(n)}(a) - K_\infty^{(n-1)}(a)\right|\right). \quad (4)$$

According to Erdèlyi [2], a power series, such as equation (16) of I, is said to be asymptotically convergent to $S(z)$ if the error which results from replacing the function $S(z)$ of the complex variable z by the partial sum $S_n(z)$ of the same series is infinitesimal of an order higher than the last term of the partial sum when $z \to \infty$. The reader might consult [3] for a general exposition of the principles underlying the asymptotic evaluation of integrals like (1).

We begin to prove the asymptotic nature of the formula for evaluating the Keesom integral up to the first term of the expansion. Putting

$$\left|\Delta_{\infty}^{(n)}(a)\right| = -\frac{a}{2}\exp\{2a\}\left|\Delta K_{\infty}^{(n)}(a)\right|, \tag{5}$$

we proceed to find a bound for the quantity

$$|\Delta^{(1)}(a)| = \left|\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \int_0^{\pi} \mathrm{d}\alpha \int_0^{\alpha} \mathrm{d}\beta \left[\exp\{a(2+F(\Omega))\} \right.\right.$$
$$\left.\left. - \exp\left\{\frac{a}{2}\left(1+\frac{\cos\varphi}{2}\right)\alpha^2 + \frac{a}{2}\left(1-\frac{\cos\varphi}{2}\right)\beta^2\right\}\right]\right|. \tag{6}$$

In equation (6) the integral over $\mathrm{d}\varphi$ in the rhs is a curvilinear integral along a curve in the complex plane as specified above (see section 1). The integrand is holomorphic in an open connected subset of the complex plane and therefore it admits a primitive along C [4], which coincides with the primitive of the integrand. This allows us, by parametrizing the integral along the curve C, to obtain the bounds as shown below and in equation (16).

$\Delta^{(1)}(a)$ differs from $\Delta_{\infty}^{(1)}(a)$ by exponentially small terms (see I). By inverting the order of integration and renaming the variables, $\Delta^{(1)}(a)$ may be rewritten in the following form (see equation (24)):

$$|\Delta^{(1)}(a)| = \left|\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi}\left[\int_0^{\pi} \mathrm{d}\alpha \int_0^{\alpha} \mathrm{d}\beta \left(\exp\{a(2+F(\Omega))\} - \exp\left\{\frac{a}{2}\left(1+\frac{\cos\varphi}{2}\right)\alpha^2\right.\right.\right.\right.$$
$$\left.\left. + \frac{a}{2}\left(1-\frac{\cos\varphi}{2}\right)\beta^2\right\}\right) - \int_0^{\pi} \mathrm{d}\alpha \int_{\alpha}^{\pi} \mathrm{d}\beta \left(\exp\{a(2+F(\Omega))\}\right.$$
$$\left.\left.\left. - \exp\left\{\frac{a}{2}\left(1+\frac{\cos\varphi}{2}\right)\alpha^2 + \frac{a}{2}\left(1-\frac{\cos\varphi}{2}\right)\beta^2\right\}\right)\right]\right|$$
$$< \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \left|\mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi}\right| \int_0^{\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \left| \exp\{a(2+F(\Omega))\}\right.$$
$$\left. - \exp\left\{\frac{a}{2}\left(1+\frac{\cos\varphi}{2}\right)\alpha^2 + \frac{a}{2}\left(1-\frac{\cos\varphi}{2}\right)\beta^2\right\}\right|, \tag{7}$$

where the following inequalities hold for real arguments:

$$a(2+F(\Omega)) = a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha) + a\left(1-\frac{\cos\varphi}{2}\right)(1-\cos\beta)$$
$$> a\sum_{m=1}^{n(\mathrm{odd})}(-1)^{m-1}\left[\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^{2m}}{(2m)!} + \left(1-\frac{\cos\varphi}{2}\right)\frac{\beta^{2m}}{(2m)!}\right], \tag{8}$$

together with the reversed ones for n even.

3. Bound to the integral over dα

Consequently, we are led to find a bound to the quantity

$$\int_0^{\pi} \mathrm{d}\alpha \left| \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\} - \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|$$
$$= \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left| \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\} - \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|$$
$$+ \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\} - \exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|$$

$$
\begin{aligned}
&< \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right) \right.\right. \\
&\quad \times \left.\left.\left(1-\cos\alpha-\frac{\alpha^2}{2}\right)\right\}-1\right| + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\}\right| \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| < \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left| a\left(1+\frac{\cos\varphi}{2}\right)\right. \\
&\quad \times \left.\left(1-\cos\alpha-\frac{\alpha^2}{2}\right) + \frac{1}{2!}a^2\left(1+\frac{\cos\varphi}{2}\right)^2\left(1-\cos\alpha-\frac{\alpha^2}{2}\right)^2+\cdots\right| \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\}\right| \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| \leqslant \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left[\left| a\left(1+\frac{\cos\varphi}{2}\right)\right.\right. \\
&\quad \times \left.\left(1-\cos\alpha-\frac{\alpha^2}{2}\right)\right| + \frac{1}{2!}\left| a\left(1+\frac{\cos\alpha}{2}\right)\left(1-\cos\varphi-\frac{\alpha^2}{2}\right)\right|^2+\cdots\Bigg] \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\}\right| \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| < \int_o^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left[\left| a\left(1+\frac{\cos\varphi}{2}\right)\right| \right. \\
&\quad \times \left. \frac{\alpha^4}{4!} + \frac{1}{2!}\left| a\left(1+\frac{\cos\varphi}{2}\right)\right|^2\left(\frac{\alpha^4}{4!}\right)^2\cdots+\frac{1}{n!}\left| a\left(1+\frac{\cos\varphi}{2}\right)\right|^n\left(\frac{\alpha^4}{4!}\right)^n+\cdots\right] \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\}\right| \\
&\quad + \int_{(-a)^{\varepsilon-1/2}}^{\pi} \mathrm{d}\alpha \left| \exp\left\{ a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| < \left|1+\frac{\cos\varphi}{2}\right| \left[\frac{(-a)^{5\varepsilon-3/2}}{5!} \right. \\
&\quad + \left|1+\frac{\cos\varphi}{2}\right| \frac{(-a)^{9\varepsilon-5/2}}{2!\times 9\times(4!)^2} + \left|1+\frac{\cos\varphi}{2}\right|^2 \frac{(-a)^{13\varepsilon-7/2}}{3!\times 13\times(4!)^3}+\cdots\Bigg] \\
&\quad + \frac{1}{(-a)\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)} \left[\frac{1}{\sqrt{\frac{(-a)^{2\varepsilon}}{2(-a)} - \frac{(-a)^{4\varepsilon}}{4!(-a)^2}}} + \frac{1}{(-a)^{\varepsilon-1/2}} \right] \\
&\quad \times \exp\left\{ -\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\left(\frac{(-a)^{2\varepsilon}}{2} - \frac{(-a)^{4\varepsilon}}{4!(-a)}\right)\right\} \\
&\quad + O\left(\exp\left\{ a\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right\}\right),
\end{aligned}
\tag{9}
$$

with $\varepsilon > 0$. In the expression above we have retained only, for every given negative power of $(-a)$, that term with the highest power of $(-a)^{\varepsilon}$.

The bound to the first integral above has been obtained by expanding the function $\cos\alpha$, and retaining only the first nonzero term in the argument of the exponential, which, according to equation (8), yields an upper bound to the absolute value of the argument, so that the exponential can be subsequently expanded with uniform convergence in the compact set: $\left\{0 \leqslant \alpha \leqslant \frac{1}{(-a)^{1/2-\varepsilon}}, 0 \leqslant \frac{1}{(-a)} \leqslant \mathrm{M}\right\}$ for $\varepsilon \leqslant \frac{1}{4}$, M real.

The bound to the second integral has been obtained by making use of the inequality

$$\int_y^{\pi/2} \mathrm{d}\alpha \exp\{a\Phi(\alpha)\} \leqslant \frac{2}{\sqrt{\pi\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)}}\left[\int_0^\infty \mathrm{d}\eta \frac{\exp\{(a-\eta^2)\Phi(y)\}}{\eta^2-a} - \int_0^\infty \mathrm{d}\eta \frac{\exp\left\{(a-\eta^2)\Phi\left(\frac{\pi}{2}\right)\right\}}{\eta^2-a}\right], \tag{10}$$

where $0 \leqslant y \leqslant \pi/2$ and

$$\Phi(\alpha) = \left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)(1-\cos\alpha). \tag{10$'$}$$

This inequality has been proved in [5] by estimating the derivatives of both members, which yields

$$-\exp\{a\Phi(y)\} \geqslant -\frac{1}{\sqrt{2}}\exp\{a\Phi(y)\}\frac{\sin y}{\sin\frac{y}{2}}. \tag{10$''$}$$

The inequality (10) is then obtained straightforwardly by integration:

$$\int_{\pi/2}^{y} \mathrm{d}\alpha \left[\exp\{a\Phi(\alpha)\} - \exp\{a\Phi(\alpha)\}\frac{\sin\alpha}{\sqrt{2}\sin\alpha/2}\right] \geqslant 0. \tag{10$'''$}$$

The analogous relation for

$$\Phi(\alpha) = \left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\frac{\alpha^2}{2} \tag{11}$$

is the following:

$$\int_y^\infty \mathrm{d}\alpha \exp\{a\Phi(\alpha)\} = \sqrt{\frac{2}{\pi\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)}}\int_0^\infty \mathrm{d}\eta \frac{\exp\{(a-\eta^2)\Phi(y)\}}{\eta^2-a}. \tag{11$'$}$$

Let us now put

$$5\varepsilon = \delta, \qquad 0 \leqslant \delta \leqslant \tfrac{5}{4}, \tag{12}$$

therefore, by repeating the argument with the negative sign, there results that

$$\begin{aligned}\int_0^\pi \mathrm{d}\alpha & \left|\exp\left\{a\left(1\pm\frac{\cos\varphi}{2}\right)(1-\cos\alpha)\right\} - \exp\left\{a\left(1\pm\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| \\ & < \left|1\pm\frac{\cos\varphi}{2}\right|\frac{1}{5!(-a)^{3/2-\delta}} + O\left(\frac{1}{(-a)^{5/2-9\delta/5}}\right) + \frac{1}{\left(1\pm\frac{\mathrm{Re}(\cos\varphi)}{2}\right)} \\ & \times \left[\frac{1}{\sqrt{\frac{(-a)^{1+2\delta/5}}{2} - \frac{(-a)^{4\delta/5}}{4!}}} + \frac{1}{(-a)^{1/2+\delta/5}}\right]\exp\left\{-\left(1\pm\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right. \\ & \times \left.\left(\frac{(-a)^{2\delta/5}}{2} - \frac{(-a)^{4\delta/5-1}}{4!}\right)\right\} + O\left(\exp\left\{a\left(1\pm\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right\}\right).\end{aligned} \tag{13}$$

4. A bound to $\Delta^{(1)}(a)$

Now we make use of the following identities among the quantities X, $X^{(0)}$, Y, $Y^{(0)}$, which are represented by real or complex numbers:

$$XY - X^{(0)}Y^{(0)} = (X - X^{(0)})Y + X^{(0)}(Y - Y^{(0)}) = (X - X^{(0)})Y^{(0)} + X(Y - Y^{(0)}), \tag{14}$$

so as to obtain, making use of equations (10), (13) and the first identity above,

$$\begin{aligned}
&\int_0^\pi \mathrm{d}\alpha \int_0^\pi \mathrm{d}\beta \left| \exp\{a\,(2 + F(\Omega))\} - \exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2} + a\left(1 - \frac{\cos\varphi}{2}\right)\frac{\beta^2}{2}\right\}\right| \\
&\quad = \int_0^\pi \mathrm{d}\alpha \int_0^\pi \mathrm{d}\beta \left|\left[\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)(1 - \cos\alpha)\right\} - \exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right]\right. \\
&\qquad \times \exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)(1 - \cos\beta)\right\} + \exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\} \\
&\qquad \left.\times \left[\exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)(1 - \cos\beta)\right\} - \exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)\frac{\beta^2}{2}\right\}\right]\right| \\
&\quad < \int_0^\pi \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)(1 - \cos\alpha)\right\} - \exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| \\
&\qquad \times \int_0^\pi \mathrm{d}\beta \exp\left\{a\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)(1 - \cos\beta)\right\} \\
&\qquad + \int_0^\pi \mathrm{d}\alpha \exp\left\{a\left(1 + \frac{\mathrm{Re}(\cos\varphi)}{2}\right)\frac{\alpha^2}{2}\right\} \\
&\qquad \times \int_0^\pi \mathrm{d}\beta \left|\exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)(1 - \cos\beta)\right\} - \exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)\frac{\beta^2}{2}\right\}\right| \\
&\quad < \left[\frac{1}{5!}\left|1 + \frac{\cos\varphi}{2}\right|\frac{1}{(-a)^{3/2-\delta}} + O\left(\frac{1}{(-a)^{5/2-9\delta/5}}\right)\right. \\
&\qquad + \frac{1}{(-a)^{1/2+\delta/5}\left(1 + \frac{\mathrm{Re}(\cos\varphi)}{2}\right)}\left(\frac{\sqrt{2}}{\sqrt{1 - \frac{(-a)^{2\delta/5-1}}{12}}} + 1\right) \\
&\qquad \times \exp\left\{-\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)\left(\frac{(-a)^{2\delta/5}}{2} - \frac{(-a)^{4\delta/5}}{4!(-a)}\right)\right\} \\
&\qquad \left. + O\left(\exp\left\{a\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right\}\right)\right] \times \left[\sqrt{\frac{\pi}{-a\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)}}\right. \\
&\qquad \left. + O\left(\exp\left\{a\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right\}\right)\right] + \left[\frac{1}{5!}\left|1 - \frac{\cos\varphi}{2}\right|\frac{1}{(-a)^{3/2-\delta}}\right. \\
&\qquad + O\left(\frac{1}{(-a)^{5/2-9\delta/5}}\right) + \frac{1}{(-a)^{1/2+\delta/5}\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)}\left(\frac{\sqrt{2}}{\sqrt{1 - \frac{(-a)^{2\delta/5-1}}{12}}} + 1\right) \\
&\qquad \times \exp\left\{-\left(1 - \frac{\mathrm{Re}(\cos\varphi)}{2}\right)\left(\frac{(-a)^{2\delta/5}}{2} - \frac{(-a)^{4\delta/5}}{4!(-a)}\right)\right\}
\end{aligned}$$

$$
+\,O\left(\exp\left\{a\left(1-\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\right\}\right)\Bigg]\times\frac{1}{2}\times\sqrt{\frac{2\pi}{-a\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)}}
$$

$$
<\sqrt{\pi}\left[\frac{\left|1+\frac{\cos\varphi}{2}\right|}{\sqrt{1-\frac{\mathrm{Re}(\cos\varphi)}{2}}}+\frac{\left|1-\frac{\cos\varphi}{2}\right|}{\sqrt{2\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)}}\right]\left[\frac{1}{5!(-a)^{2-\delta}}+O\left(\frac{1}{(-a)^{3-9\delta/5}}\right)\right]
$$

$$
+\frac{\sqrt{\pi}}{(-a)^{1+\delta/5}}\left[\frac{\sqrt{2}}{\sqrt{1-\frac{(-a)^{2\delta/5-1}}{12}}}+1\right]\frac{\exp\left\{-\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\left(\frac{(-a)^{2\delta/5}}{2}-\frac{(-a)^{4\delta/5}}{4!(-a)}\right)\right\}}{\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\sqrt{1-\frac{\mathrm{Re}(\cos\varphi)}{2}}}
$$

$$
+\frac{\sqrt{\frac{\pi}{2}}}{(-a)^{1+\delta/5}}\left[\frac{\sqrt{2}}{\sqrt{1-\frac{(-a)^{2\delta/5-1}}{12}}}+1\right]\frac{\exp\left\{-\left(1-\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\left(\frac{(-a)^{2\delta/5}}{2}-\frac{(-a)^{4\delta/5}}{4!(-a)}\right)\right\}}{\left(1-\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\sqrt{1+\frac{\mathrm{Re}(\cos\varphi)}{2}}}
$$

$$
+\,O\left(\exp\left\{a\left(1-\frac{|\mathrm{Re}(\cos\varphi)|}{2}\right)\right\}\right). \tag{15}
$$

By making use of the second identity (14), an inequality similar to (15) is obtained, with $\cos\varphi$ interchanged with $-\cos\varphi$.

As a last step, we find a bound for the quantity $|\Delta^{(1)}(a)|$ of equation (7), by defining an appropriate path joining the points $-\frac{\pi}{2}, \frac{\pi}{2}$ in the complex plane of the variable φ, satisfying the conditions stated in the introduction. Then, it results from (7) that

$$
|\Delta^{(1)}(a)| < \int_{\mathrm{C}}\left|\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\right|\left|\int_0^{\pi}\mathrm{d}\alpha\int_0^{\pi}\mathrm{d}\beta\right|\exp\{a(2+F(\Omega))\}
$$

$$
-\exp\left\{\frac{a}{2}\left(1+\frac{\cos\varphi}{2}\right)\alpha^2+\frac{a}{2}\left(1-\frac{\cos\varphi}{2}\right)\beta^2\right\}\Bigg|. \tag{16}
$$

C is the semicircle inside the complex plane of the variable $\frac{1}{\sin\varphi}$, with modulus 1, centred in the origin and joining the points -1 and 1. Putting $\sin\varphi=\rho\,\mathrm{e}^{\mathrm{i}\vartheta}$, then the curve C can be parametrized by the variable ϑ running from 0 to π. The condition $\rho=1$ reads, on putting $\varphi=\mu+\mathrm{i}\nu$ with μ, ν real,

$$
|\sin\varphi|^2=\sin^2\mu\cosh^2\nu+\cos^2\mu\sinh^2\nu=\sin^2\mu+\sinh^2\nu=1. \tag{17}
$$

By expanding the sinus functions it results that the curve C is approximately a half-circle centred in the origin, flattened in the direction of the imaginary axis and elongated along the real axis. This curve is homotopic to the interval $\left(-\frac{\pi}{2},\frac{\pi}{2}\right)$ of the real axis [4].

The condition fulfilled by a pole appearing in equation (3), mentioned in the introduction, namely $|\mathrm{Re}(\cos\varphi)|\geqslant 2$, written in the variables μ, ν becomes

$$
\cosh^2\nu\geqslant 4 \qquad \text{or} \qquad \sinh^2\nu\geqslant 3, \tag{18}
$$

which is a straight line parallel to the real φ-axis, situated well outside the semicircle C. Now using the parametrization of C, it is obtained that

$$
\int_{\mathrm{C}}\left|\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\right|=\int_{\mathrm{C}}\left|\mathrm{d}\left(\frac{1}{\sin\varphi}\right)\right|=\int_{\mathrm{C}}\left|\mathrm{d}\left(\frac{\mathrm{e}^{-\mathrm{i}\theta}}{\rho}\right)\right|\leqslant\int_{\mathrm{C}}\left(\frac{|\mathrm{d}\rho|}{\rho^2}+\frac{|\mathrm{d}\theta|}{\rho}\right)=\int_{\mathrm{C}}|\mathrm{d}\theta|, \tag{19}
$$

$$
\sin\varphi=\mathrm{e}^{\mathrm{i}\vartheta}, \qquad \cos\varphi=\pm\sqrt{\sin\vartheta}\left(\sqrt{1+\sin\vartheta}-\mathrm{i}\sqrt{1-\sin\vartheta}\right), \tag{20}
$$

consequently, by maximizing every term of equation (15) independently of the others, after optimizing the common factor under square root multiplying the exponentials, there follows, taking the upper sign in equation (20),

$$\begin{aligned}\left|\Delta_\infty^{(1)}(a)\right| &< \int_0^\pi \mathrm{d}\vartheta \int_0^\pi \mathrm{d}\alpha \int_0^\pi \mathrm{d}\beta \Big| \exp\{a(2+F(\Omega)\} \\ &\quad - \exp\left\{\frac{a}{2}(\alpha^2+\beta^2) + \frac{a}{4}\sqrt{-2\mathrm{i}\sin\vartheta\,\mathrm{e}^{\mathrm{i}\vartheta}}(\alpha^2-\beta^2)\right\}\Big| \\ &< \left[\sqrt{\frac{3+2\sqrt{2}}{2-\sqrt{2}}} + \frac{1}{\sqrt{2}}\right]\left[\frac{\pi^{3/2}}{5!(-a)^{2-\delta}} + O\left(\frac{1}{(-a)^{3-9\delta/5}}\right)\right] \\ &\quad + \frac{\sqrt{2}\pi^{3/2}}{(-a)^{1+\delta/5}}\left[\frac{\sqrt{2}}{\sqrt{1-\frac{(-a)^{2\delta/5}}{12(-a)}}} + 1\right] \\ &\quad \times \left[\frac{1}{\sqrt{2-\sqrt{2}}}\exp\left\{-(2-\sqrt{2})\frac{(-a)^{2\delta/5}}{4}\left(1-\frac{(-a)^{2\delta/5}}{12(-a)}\right)\right\}\right. \\ &\quad \left. + \exp\left\{-\frac{(-a)^{2\delta/5}}{2}\left(1-\frac{(-a)^{2\delta/5}}{12(-a)}\right)\right\}\right] + O\left(\exp\left\{\frac{a}{2}(2-\sqrt{2})\right\}\right). \end{aligned} \tag{21}$$

A slightly different bound is obtained by selecting the lower sign in (20). Now, in order to obtain a bound on the error in $K(a)$, the Keesom integral [1], we must write

$$\left|\Delta K_\infty^{(1)}(a)\right| = 2\frac{\exp\{-2a\}}{(-a)}\left|\Delta_\infty^{(1)}(a)\right| = o\left(\frac{\mathrm{e}^{-2a}}{a^2}\right), \tag{22}$$

which yields the necessary estimate, in order that $K_\infty^{(1)}(a)$ should be an asymptotic representation.

5. Sketch of the general proof for $\Delta K_\infty^{(n)}(a)$

We present here the lines along which the proof can be generalized to the partial sums $K_\infty^{(n)}(a)$ defined by equation (3). Let us define, for $n \geqslant 1$,

$$\begin{aligned} A^{(n)}(\xi,a) &= \exp\left\{-\left(1+\frac{\cos\varphi}{2}\right)\frac{\xi^2}{2}\right\}\sum_{\nu=0}^{n}\frac{(-1)^\nu}{(-a)^\nu}\sum_{\lambda=0}^{\nu}\frac{(-1)^\lambda}{\lambda!}\left(1+\frac{\cos\varphi}{2}\right)^\lambda \xi^{2(\lambda+\nu)} \\ &\quad \times \sum_{n_1\geqslant 2}\sum_{n_2\geqslant 2}\cdots\sum_{n_\lambda\geqslant 2}\frac{1}{(2n_1)!(2n_2)!\cdots(2n_\lambda)!}\delta_{n_1+n_2+\cdots+n_\lambda,\nu+\lambda}, \end{aligned} \tag{23}$$

where

$$\xi(\alpha) = \sqrt{-a}\alpha,$$

and similarly we call $B^{(n)}(\eta,a)$ the analogous expression where $-\cos\varphi$ and η have been substituted for $\cos\varphi$ and ξ, respectively.

Then, we have

$$\begin{aligned} |\Delta^{(n)}(a)| &= \Big|\int_{-\pi/2}^{3\pi/2}\mathrm{d}\varphi\frac{\cos\varphi}{\sin^2\varphi}\int_0^\pi \mathrm{d}\alpha\int_0^\alpha \mathrm{d}\beta\Big[\exp\{a(2+F(\Omega))\} \\ &\quad - A^{(n-1)}(\xi(\alpha),a)B^{(n-1)}(\eta(\beta),a) \\ &\quad + \sum_{m=1}^{n-1} O\left(\frac{\xi^{4m}\eta^{4(n-m)}\,\mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n}\right)\Big]\Big| \end{aligned}$$

$$
\begin{aligned}
&= \Bigg| \int_{-\pi/2}^{\pi/2} \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \Bigg[\int_0^{\pi} \mathrm{d}\alpha \int_0^{\alpha} \mathrm{d}\beta \Bigg(\exp\Bigg\{ a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)(1 - \cos\alpha) \\
&\quad + a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} - A^{(n-1)}(\xi(\alpha), a) B^{(n-1)}(\eta(\beta), a) \Bigg) \\
&\quad - \int_0^{\pi} \mathrm{d}\beta \int_{\beta}^{\pi} \mathrm{d}\alpha \Bigg(\exp\Bigg\{ a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\alpha) \\
&\quad + a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} - B^{(n-1)}(\eta(\alpha), a) A^{(n-1)}(\xi(\beta), a) \\
&\quad + \sum_{m=1}^{n-1} O\Bigg(\frac{\xi^{4m} \eta^{4(n-m)} \, \mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n} \Bigg) \Bigg) \Bigg] \Bigg| \\
&< \int_{-\pi/2}^{\pi/2} \Bigg| \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \Bigg| \Bigg[\Bigg| \int_0^{\pi} \mathrm{d}\alpha \int_0^{\alpha} \mathrm{d}\beta \Bigg(\exp\Bigg\{ a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)((1 - \cos\alpha)) \\
&\quad + a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} - A^{(n-1)}(\xi(\alpha), a) B^{(n-1)}(\eta(\beta), a) \\
&\quad + \sum_{m=1}^{n-1} O\Bigg(\frac{\xi^{4m} \eta^{4(n-m)} \, \mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n} \Bigg) \Bigg) \Bigg| \\
&\quad + \Bigg| \int_0^{\pi} \mathrm{d}\alpha \int_{\alpha}^{\pi} \mathrm{d}\beta \Bigg(\exp\Bigg\{ a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)(1 - \cos\alpha) \\
&\quad + a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} - A^{(n-1)}(\xi(\alpha), a) B^{(n-1)}(\eta(\beta), a) \\
&\quad + \sum_{m=1}^{n-1} O\Bigg(\frac{\xi^{4m} \eta^{4(n-m)} \, \mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n} \Bigg) \Bigg) \Bigg| \Bigg] \\
&< \int_{-\pi/2}^{\pi/2} \Bigg| \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \Bigg| \int_0^{\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \Bigg| \exp\{a(2 + F(\Omega))\} \\
&\quad - A^{(n-1)}(\xi(\alpha), a) B^{(n-1)}(\eta(\beta), a) + \sum_{m=1}^{n-1} O\Bigg(\frac{\xi^{4m} \eta^{4(n-m)} \, \mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n} \Bigg) \Bigg| \\
&= \int_{-\pi/2}^{\pi/2} \Bigg| \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \Bigg| \int_0^{\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \Bigg| \Bigg[\exp\Bigg\{ a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)(1 - \cos\alpha) \Bigg\} \\
&\quad - A^{(n-1)}(\xi(\alpha), a) \Bigg] \exp\Bigg\{ a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} + A^{(n-1)}(\xi(\alpha), a) \\
&\quad \times \Bigg[\exp\Bigg\{ a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} - B^{(n-1)}(\eta(\beta), a) \Bigg] \\
&\quad + \sum_{m=1}^{n-1} O\Bigg(\frac{\xi^{4m} \eta^{4(n-m)} \, \mathrm{e}^{-(\xi^2+\eta^2)(2-\sqrt{2})/4}}{(-a)^n} \Bigg) \Bigg| \\
&\leqslant \int_{-\pi/2}^{\pi/2} \Bigg| \mathrm{d}\varphi \frac{\cos\varphi}{\sin^2\varphi} \Bigg| \Bigg[\int_0^{\pi} \mathrm{d}\alpha \Bigg| \exp\Bigg\{ a\Bigg(1 + \frac{\cos\varphi}{2}\Bigg)(1 + \cos\alpha) \Bigg\} \\
&\quad - A^{(n-1)}(\xi(\alpha), a) \Bigg| \int_0^{\pi} \mathrm{d}\beta \Bigg| \exp\Bigg\{ a\Bigg(1 - \frac{\cos\varphi}{2}\Bigg)(1 - \cos\beta) \Bigg\} \Bigg|
\end{aligned}
$$

$$+ \int_0^\pi \mathrm{d}\alpha |A^{(n-1)}(\xi(\alpha), a)| \int_0^\pi \mathrm{d}\beta \bigg| \exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)(1 - \cos\beta)\right\}$$
$$- B^{(n-1)}(\eta(\beta), a)\bigg| + \frac{1}{(-a)^n} \sum_{m=1}^{n-1} \int_0^\pi \mathrm{d}\alpha\, O\big(\xi^{4m}\, \mathrm{e}^{-\xi^2(2-\sqrt{2})/4}\big)$$
$$\times \int_0^\pi \mathrm{d}\beta\, O\eta^{4(n-m)}\, \mathrm{e}^{-\eta^2(2-\sqrt{2})/4}\bigg]. \qquad (24)$$

Therefore, we need to find a bound to the quantities

$$\int_0^\pi \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)(1 - \cos\alpha)\right\} - A^{(n-1)}(\xi(\alpha), a)\right|, \qquad (25)$$

$$\int_0^\pi \mathrm{d}\beta \left|\exp\left\{a\left(1 - \frac{\cos\varphi}{2}\right)(1 - \cos\beta)\right\}\right|, \qquad \int_0^\pi \mathrm{d}\alpha |A^{(n-1)}(\xi(\alpha), a)| \qquad (25')$$

(and the analogue for $B^{(n-1)}$ replacing $A^{(n-1)}$) by splitting, as before, the domain of integration into subintervals. First, we have

$$\int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)(1 - \cos\alpha)\right\} - A^{(n-1)}(\xi(\alpha), a)\right|$$
$$\leqslant \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|$$
$$\times \left|\exp\left\{\left(1 + \frac{\cos\varphi}{2}\right)\left(\frac{\xi^4}{4!(-a)} - \cdots + (-1)^n \frac{\xi^{2n}}{(2n)!(-a)^{n-1}} + \cdots\right)\right\}\right.$$
$$\left. - A^{(n-1)}(\xi(\alpha), a) \exp\left\{-a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|$$
$$= \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right| \left|\sum_{\kappa=0}^{\infty} \frac{\left(1 + \frac{\cos\varphi}{2}\right)^\kappa}{\kappa!}\right.$$
$$\times \left(\frac{\xi^4}{4!(-a)} - \frac{\xi^6}{6!(-a)^2} + \cdots + (-1)^n \frac{\xi^{2n}}{(2n)!(-a)^{n-1}} + \cdots\right)^\kappa - \sum_{\lambda=0}^{n-1} \frac{\left(1 + \frac{\cos\varphi}{2}\right)^\lambda}{\lambda!}$$
$$\left.\times \left(\frac{\xi^4}{4!(-a)} - \frac{\xi^6}{6!(-a)^2} + \cdots + (-1)^n \frac{\xi^{2n}}{(2n)!(-a)^{n-1}}\right)^\lambda + O\left(\frac{\xi^{4n-2}}{(-a)^n}\right)\right|. \qquad (26)$$

There results, after cancellation of all the terms of the expansion by those which appear in $A^{(n-1)}(\xi, a)$, and retaining only one term inside the parenthesis for $\kappa \geqslant n$ (see inequality (8)), that

$$\int_0^{(-a)^{-1/2+\varepsilon}} \mathrm{d}\alpha \left|\exp\left\{a\left(1 + \frac{\cos\varphi}{2}\right)(1 - \cos\alpha)\right\} - A^{(n-1)}(\xi(\alpha), a)\right|$$
$$< \int_0^{(-a)^{-1/2+\varepsilon}} \mathrm{d}\alpha \left|\exp\left\{\left(1 + \frac{\cos\varphi}{2}\right)\left(-\frac{\xi^2}{2}\right)\right\}\right|$$
$$\times \left|\sum_{m=n}^{\infty} \frac{1}{m!}\left(1 + \frac{\cos\varphi}{2}\right)^m \left(\frac{\xi^4}{4!(-a)} - \frac{\xi^6}{6!(-a)^2} + \cdots\right.\right.$$
$$\left.\left. + (-1)^n \frac{\xi^{2n}}{(2n)!(-a)^{n-1}} + \cdots\right)^m + O\left(\frac{\xi^{4n-2}}{(-a)^n}\right)\right|$$

$$< \frac{1}{\sqrt{-a}} \int_0^{(-a)^{\varepsilon}} \mathrm{d}\xi \left[\sum_{m=n}^{\infty} \frac{1}{m!} \left| 1 + \frac{\cos\varphi}{2} \right|^m \left(\frac{\xi^4}{4!(-a)} \right)^m + O\left(\frac{\xi^{4n-2}}{(-a)^n} \right) \right]$$

$$= \frac{1}{\sqrt{-a}} \sum_{m=n}^{\infty} \frac{1}{m!} \left| 1 + \frac{\cos\varphi}{2} \right|^m \frac{(-a)^{(4m+1)\varepsilon}}{(4m+1)(4!)^m(-a)^m} + O\big((-a)^{(4n-1)\varepsilon - n - \frac{1}{2}}\big). \tag{27}$$

The bounds upon the quantities labelled (25′) may be obtained from equations (10) and (11′). Now upon substitution into equation (24), the bound for $\Delta_{\infty}^{(n)}(a)$ is obtained, which differs from $\Delta^{(n)}(a)$ by a finite sum of exponentially small terms (see equation (15) of I):

$$\left|\Delta_{\infty}^{(n)}(a)\right| = O((-a)^{(4n+1)\varepsilon - n - 1}), \tag{28}$$

which is the estimate that is needed in order to prove the asymptotic expansion, for $0 < \varepsilon < 1/(4n+1)$.

6. Conclusions

In paper I and in the present one, we have examined the problem of evaluating in an accurate way the partition function of a couple of dipoles interacting through electromagnetic forces, in the range of low temperature and short distances, characterized by large values of the parameter $-a$. The spatial configurational factor of the partition function is called the Keesom integral over the mutual angular orientations of the dipoles, and it results therefore the integral of a periodic function of the angular variables defining the orientations. For low values of the parameter $-a$, the exponential can be expanded, as shown by Keesom in 1921, but the convergence is not uniform as the parameter $-a$ increases, so that a very large number of terms are needed even at moderately large values of this parameter so as to obtain accurate results. For this reason, in our paper I we have retained the harmonic approximation of the interaction potential expanded around the stable equilibrium positions corresponding to zero temperature and short distances (or $a = -\infty$). The (infinite) anharmonic corrections to this ideal situation are subsequently taken into account by an infinite series expansion, which is amenable to analytical calculation to all orders. That series however is fraught with difficulties in much the same way as the complete expansion mentioned above, because an increasingly large number of terms is necessary to approximate the given function within a predetermined accuracy in a given interval of values of the angular variables. For this reason, a proof is needed to show that the integral of any finite number of terms of this series (see equation (15) of I) is asymptotically convergent to the Keesom integral, in the sense specified by equations (4) and (28) of this paper. This property is not trivial since, as noticed above, the series expansion is not convergent uniformly in the whole interval to the limit function as $a \to -\infty$.

However, as a consequence to the proof given here, a finite number of terms of the series is sufficient to give a value of the Keesom integral asymptotically exact, in the sense specified by Erdèlyi [2]. As a consequence of this, the border terms which result from the integration over the angles can be neglected, because they are exponentially infinitesimal as $-a$ goes to infinity. Although it is actually divergent as $n \to \infty$, we have proved that the expansion (3) of the present paper is therefore an asymptotic expansion.

It has therefore been rigorously proved the validity of the harmonic approximation to the interaction potential, conformly to physical intuition, and for this model a bound is given for the error, which, though not really optimal, is however expected to be rather close to the truth for physically easily accessible values of a (see table 1 in I).

For the general anharmonic case it is proved the asymptotic convergence only, the error being bounded by a function which is infinitesimal for increasingly higher values of $-a$ as $n \to \infty$, which means that the asymptotic convergence is *not uniform* with respect to n.

Acknowledgments

Support by the Italian Ministry of Education University and Research (MIUR) under grant no 2004 03 4838 009 and by the University of Genoa is gratefully acknowledged.

Appendix

The inequality which has been obtained depends upon ε, but, while the first term which is asymptotically dominating improves as $\varepsilon \to 0$, the remaining terms worsen as ε decreases, so that ε cannot be put too small. A referee of this article has pointed out, by a different estimate of the factors inside the integral in equation (9) of the paper, that these bounds can be improved (his calculations correspond to $\varepsilon = \frac{1}{6}$). Actually, since we have proved (equation (26) of the paper) the asymptotic convergence of the sequence of functions $K_\infty^{(n)}(a)$ for every n (though not uniformly in n), there follows (Erdèlyi [2] p 13, equation (6)) that the error affecting the asymptotic representation $K_\infty^{(1)}(a)$ is $O\left(\frac{1}{|a|^3}\right)$ instead of $O\left(\frac{1}{|a|^{3-\delta}}\right)$.

In order to overcome this inconsistency, we show that this result can be proved here straightforwardly by rearranging the factors in equation (9):

$$\begin{aligned}
&\int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left|\exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\}\right|\left|\exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\left(1-\cos\alpha-\frac{\alpha^2}{2}\right)\right\}-1\right| \\
&\quad\leqslant \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \left|\exp\left\{a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^2}{2}\right\} a\left(1+\frac{\cos\varphi}{2}\right)\frac{\alpha^4}{4!}\right| \\
&\quad\times\left[1+\frac{1}{2!}\left|a\left(1+\frac{\cos\varphi}{2}\right)\right|\frac{\alpha^4}{4!}+\cdots+\frac{1}{n!}\left|a\left(1+\frac{\cos\varphi}{2}\right)\right|^{n-1}\left(\frac{\alpha^4}{4!}\right)^{n-1}+\cdots\right] \\
&\quad< \int_0^{(-a)^{\varepsilon-1/2}} \mathrm{d}\alpha \exp\left\{a\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)\frac{\alpha^2}{2}\right\}\left|a\left(1+\frac{\cos\varphi}{2}\right)\right|\frac{\alpha^4}{4!} \\
&\quad\times\left[1+\frac{1}{2!}\left|a\left(1+\frac{\cos\varphi}{2}\right)\right|\frac{(-a)^{4\varepsilon-2}}{4!}+\cdots+\frac{1}{n!}\right. \\
&\quad\times\left.\left|a\left(1+\frac{\cos\varphi}{2}\right)\right|^{n-1}\frac{(-a)^{4(n-1)\varepsilon-2(n-1)}}{(4!)^{n-1}}+\cdots\right] \\
&\quad< \frac{1}{8}\sqrt{\frac{\pi}{2}}\frac{\left|1+\frac{\cos\varphi}{2}\right|}{(-a)^{3/2}\left(1+\frac{\mathrm{Re}(\cos\varphi)}{2}\right)^{5/2}}[1+O((-a)^{4\varepsilon-1})].
\end{aligned} \tag{A.1}$$

Thus, the first term of our bound (9) can be made totally independent of ε allowing us to put ε equal to its maximum value (12) which satisfies the required conditions of uniform convergence of the factor inside the square brackets.

However, the estimate that we have obtained in the paper is correct because every term under the integral sign is bounded properly: the replacement of the Gaussian factor by unity is a bound, not an expansion. Nevertheless, the estimate is not optimal, because that first (Gaussian-shaped) factor cannot be expanded and integrated term by term with uniform convergence with respect to a, *for any value of* $\varepsilon > 0$: the series obtained in this way, though convergent, is not of the order of magnitude of its first term, because, since it does not converge uniformly with respect to a, it cannot be approximated by a finite number of terms independently of a. There follows that the correct (optimal) result is obtained in the way displayed in this appendix, and it leads to the correct dependence on $\frac{1}{|a|}$ of the error affecting the asymptotic representation.

The procedure that we have adopted in section 2 of this paper is however much simpler and easily generalized to higher orders, though leading to qualitatively equivalent results. Moreover, it yields a sensibly smaller coefficient multiplying the leading asymptotic term.

Post-scriptum

It was observed by a referee that the presentation of equation (8) of I is unclear. To avoid misunderstanding by the readers, we enclose here a detailed proof of the first line of this equation.

The Keesom integral is written, according to our definitions (1), (2), (2′) and (2″) in the form

$$\begin{aligned}K(a) &= \int_S \mathrm{d}\Omega\ \exp[aF(\Omega)] \\ &= \int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta_A \sin\theta_A \int_0^{\pi} \mathrm{d}\theta_B \sin\theta_B \exp\{a(\sin\theta_A \sin\theta_B \cos\varphi - 2\cos\theta_A \cos\theta_B)\} \\ &= \int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta_A \int_0^{\pi} \mathrm{d}\theta_B \left(-\frac{1}{a\sin\varphi}\right) \frac{\partial}{\partial\varphi} \exp\{a(\sin\theta_A \sin\theta_B \cos\varphi - 2\cos\theta_A \cos\theta_B)\}.\end{aligned}$$

Since the integral converges absolutely in the square $0 \leqslant \theta_A, \theta_B \leqslant \pi$ and the integrand is continuously differentiable, it is possible to write

$$K(a) = \int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} \mathrm{d}\varphi \left(-\frac{1}{a\sin\varphi}\right) \frac{\partial}{\partial\varphi} \int_0^{\pi} \mathrm{d}\theta_A \int_0^{\pi} \mathrm{d}\theta_B \exp\{a(\sin\theta_A \sin\theta_B \cos\varphi - 2\cos\theta_A \cos\theta_B)\}.$$

Now we change to new variables

$$\begin{cases}\alpha = \theta_B + \theta_A, \\ \beta = \theta_B - \theta_A,\end{cases}$$

with the inverse transformation

$$\begin{cases}\theta_A = \frac{1}{2}(\alpha - \beta), \\ \theta_B = \frac{1}{2}(\alpha + \beta),\end{cases}$$

where (see figure 1 of I)

$$\begin{aligned}&0 \leqslant \alpha \leqslant \pi, && -\alpha \leqslant \beta \leqslant \alpha, \\ &\pi \leqslant \alpha \leqslant 2\pi, && (\alpha - 2\pi) \leqslant \beta \leqslant (2\pi - \alpha),\end{aligned}$$

so that $F(\Omega)$ becomes

$$F(\Omega) = \tfrac{1}{2}(\cos\beta - \cos\alpha)\cos\varphi - (\cos\beta + \cos\alpha).$$

The Jacobian of the transformation is

$$\begin{vmatrix}\frac{\partial\theta_A}{\partial\alpha} & \frac{\partial\theta_A}{\partial\beta} \\ \frac{\partial\theta_B}{\partial\alpha} & \frac{\partial\theta_B}{\partial\beta}\end{vmatrix} = \begin{vmatrix}\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2}\end{vmatrix} = \frac{1}{2},$$

so that

$$\int_0^{\pi} d\theta_A \int_0^{\pi} d\theta_B = \frac{1}{2}\int_0^{\pi} d\alpha \int_{-\alpha}^{\alpha} d\beta + \frac{1}{2}\int_{\pi}^{2\pi} d\alpha \int_{\alpha-2\pi}^{2\pi-\alpha} d\beta.$$

Therefore, it is obtained that

$$K(a) = -\frac{1}{2a}\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} d\varphi \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left[\int_0^{\pi} d\alpha \int_{-\alpha}^{\alpha} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha \right.\right.$$
$$\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\} + \int_{\pi}^{2\pi} d\alpha \int_{\alpha-2\pi}^{2\pi-\alpha} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha\right.$$
$$\left.\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\}\right].$$

Because the function $\cos\beta$ is an even function of β, there follows that the integral can also be written as

$$K(a) = -\frac{1}{a}\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} d\varphi \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left[\int_0^{\pi} d\alpha \int_0^{\alpha} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha \right.\right.$$
$$\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\} + \int_{\pi}^{2\pi} d\alpha \int_0^{2\pi-\alpha} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha\right.$$
$$\left.\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\}\right].$$

Now we introduce the new variable

$$\mu = 2\pi - \alpha,$$

so as to obtain

$$K(a) = -\frac{1}{a}\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} d\varphi \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left[\int_0^{\pi} d\alpha \int_0^{\alpha} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha \right.\right.$$
$$\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\} + \int_{\pi}^{0} d(-\mu) \int_0^{\mu} d\beta \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos(2\pi-\mu)\right.$$
$$\left.\left. -a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\}\right] = -\frac{2}{a}\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} d\varphi \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left[\int_0^{\pi} d\alpha \int_0^{\alpha} d\beta \right.$$
$$\left.\times \exp\left\{-a\left(1+\frac{\cos\varphi}{2}\right)\cos\alpha - a\left(1-\frac{\cos\varphi}{2}\right)\cos\beta\right\}\right],$$

which is the first row of equation (8) of I, after substituting for $F(\Omega)$ the previous transformed expression.

References

[1] Battezzati M and Magnasco V 2004 *J. Phys. A: Math. Gen.* **37** 9677

[2] Erdèlyi A 1956 *Asymptotic Expansions* (New York: Dover) chapter I

[3] Lavrentiev M and Chabat B 1972 *Méthodes de la théorie des fonctions d'une variable complexe* (Moscow: Mir) chapter V, p 473

[4] Cartan H 1961 *Théorie élémentaire des fonctions analytiques d'une ou plusieurs variables complexes* (Paris: Hermann) chapter II

[5] Battezzati M 1999 *J. Chem. Phys.* **111** 9932