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COMMENT

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Abstract

The asymptotic evaluation and expansion of the Keesom integral, $K(a)$, is discussed at some length in Battezzati and Magnasco (2004 *J. Phys. A: Math. Gen.* **37** 9677; 2005 *J. Phys. A: Math. Gen.* **38** 6715). Here, using standard identities, it is shown that this triple integral can be reduced to a single integral from which the asymptotic behaviour is readily obtained using Laplace's method.

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The Keesom integral

The Keesom integral [3], defined by

$$K(a) = \int_0^{\pi}\int_0^{\pi}\int_0^{2\pi} \mathrm{e}^{aF(\theta_A,\theta_B,\varphi)} \sin(\theta_A)\sin(\theta_B)\,\mathrm{d}\varphi\,\mathrm{d}\theta_A\,\mathrm{d}\theta_B, \tag{1}$$

where

$$F(\theta_A,\theta_B,\varphi) = \cos(\varphi)\sin(\theta_A)\sin(\theta_B) - 2\cos(\theta_A)\cos(\theta_B),$$

arises when computing the average value of the interaction between two dipoles undergoing thermal motion. The angles θ_A, θ_B and φ are the angles describing the mutual orientation of the dipoles. On average, the dipole moments assume orientations leading to attraction. Note that $K(a) = K(-a)$ (put $\theta_A \to \pi - \theta_A$ or $\theta_B \to \pi - \theta_B$ and $\varphi \to \pi - \varphi$ in equation (1) and change the limits of integration accordingly).

To reduce this integral, first compute the integral over φ using equation 9.6.16 of [4],

$$\int_0^{2\pi} \mathrm{e}^{s\cos(\varphi)}\,\mathrm{d}\varphi = 2\pi I_0(s),$$

where $I_0(s)$ is a modified Bessel function of the first kind of order 0. Changing variables, $x = \cos(\theta_A)x$, $y = \cos(\theta_B)$, one obtains

$$K(a) = 2\pi\int_{-1}^{1}\int_{-1}^{1} \mathrm{e}^{-2axy} I_0\big(a\sqrt{1-x^2}\sqrt{1-y^2}\big)\,\mathrm{d}x\,\mathrm{d}y.$$

Next, using equation 6.616.5 of [5],

$$\int_{-1}^{1} \mathrm{e}^{ax} I_0(b\sqrt{1-x^2})\,\mathrm{d}x = \frac{2\sinh(\sqrt{a^2+b^2})}{\sqrt{a^2+b^2}},$$

the Keesom integral reduces to single integration,

$$K(a) = 4\pi \int_{-1}^{1} \frac{\sinh(a\sqrt{3y^2+1})}{a\sqrt{3y^2+1}}\,\mathrm{d}y = \frac{8\pi}{\sqrt{3}a}\int_{1}^{2}\frac{\sinh(at)}{\sqrt{t^2-1}}\,\mathrm{d}t.$$

No further reduction appears possible. However, computing this integral numerically is straightforward and the results agree with those in table 1 of [1]. Using Laplace's method [6] one immediately obtains the large-a asymptotic expansion directly,

$$K(a) \sim \frac{4\pi}{3}\frac{\mathrm{e}^{2a}}{a^2}\left(1 + \frac{2}{3a} + \frac{1}{a^2} + \frac{22}{9a^3} + \frac{227}{27a^4} + \cdots\right),$$

which agrees with equation (30) of [1].

Since the axially symmetric multipoles are proportional to the bipolar spherical harmonics, and the Keesom integral is just the angular average of the exponential of these multipoles, one would expect similar reductions for the generalized Keesom integrals discussed in [7].

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