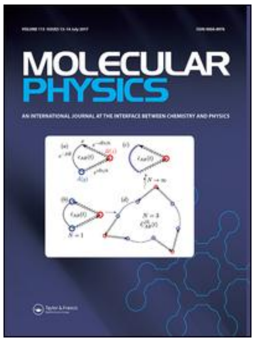

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# Effective isotropic dipole–dipole pair potential

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The orientation partition function, the associated angle-averaged Mayer $f$-function, and the effective isotropic potential for a pair of dipoles are expressed in terms of a twice-modified incomplete Struve function of zero order. The partition function is a genus one, order one, type two entire function, with an infinite number of zeros along the imaginary axis. Analytic expressions are derived that characterize it throughout the complex plane. These expressions provide efficient means for computing the partition function, the angle-averaged Mayer $f$-function, and the effective potential. The partition function's distribution of zeros and classical low-temperature behavior resemble that of the partition function for an Ising dipole pair and for a dipole in an external field, but are strikingly different from that of the Boltzmann factor of the attractive component of the Lennard-Jones effective potential of dipolar thermodynamic perturbation theory.

## 1. Introduction

The orientation partition function, angle-averaged Mayer $f$-function, and the effective isotropic potential for a pair of point dipoles feature prominently in studies of dipolar fluids. One or more of these functions appear, for example, in the theory of second virial coefficients [1, 2], in the referenced averaged Mayer $f$-function (RAM) thermodynamic perturbation theory [3], and as the potential of interaction in effective potential reference fluids [3, 4]. These functions contain angular integrals not previously integrated in terms of known functions. For explicit calculation, it has therefore been necessary to approximate them by partial sums of Maclaurin series [1, 2, 4] or by numerical integration [5, 6].

Both partial summation and numerical integration, as currently applied, are cumbersome to implement, and neither yields the classical low-temperature behaviour. Moreover, numerical integration cannot provide analytic information about these functions. Series representations can, in principle, be more helpful, since the Taylor coefficients completely specify the function's analytic character. However, little of this character is revealed by inspection of the series *per se*, although later in this paper it will be seen just how much can be inferred from a deeper analysis of these coefficients.

The chief difficulty with the series representation of the partition function and the angle-averaged $f$-function is that the Taylor coefficients are not recursively known, and are themselves sums. As more terms are needed, their computation becomes increasingly tedious. Since the effective potential is proportional to the logarithm of the partition function, its series requires yet another expansion. The finite radius of convergence of the resultant series limits its usefulness unless numerical analytic continuation schemes are devised [4].

The chief difficulty with numerical integration is that its use requires evaluation of a three-dimensional integral for each distance separating the dipoles, as well as for each change in the temperature or dipole moment. The procedure becomes computationally intensive.

It is the purpose of this paper to provide a self-contained account of the main analytic properties of the partition function and to derive recursion relations for the Taylor coefficients, asymptotic approximations for the partition function and Taylor coefficients, and polynomial approximations for real values of the partition function. The asymptotic and polynomial approximations together with the recursion relations provide a means for computing the partition function, the Mayer *f*-function and the effective potential that is accurate and efficient.

The partition function can be expressed in terms of a modified incomplete Struve function. Numerous physical applications have been described for other members of the class of incomplete Bessel functions to which this function belongs [7]. The dipole–dipole partition function is apparently the first example of an application of an incomplete Bessel function with two imaginary arguments. Although existing tables do not permit evaluation of this function, the need for such tables is eliminated by the approximations contained in this work.

The partition function is real for real values of the independent variable. By analogy with the modified Bessel functions and the singly-modified incomplete Bessel functions, it is convenient to have a real-valued function for real values of both independent variables. Such functions have not previously been defined. For this reason, twice-modified incomplete Bessel functions are defined in the Appendix, and the partition function is expressed in terms of a twice-modified incomplete Struve function of zero order.

## 2. Analytic properties

The angle-averaged *f*-function and the effective potential are simply related to the orientation partition function $Q(z)$. Most of the ensuing analysis will therefore be presented in terms of the partition function

$$q(z) = \frac{Q(z)}{(4\pi)^2} = \langle \exp (\beta \boldsymbol{\mu}_1 \cdot \mathbf{T} \cdot \boldsymbol{\mu}_2) \rangle,$$

normalized with respect to a pair of noninteracting dipoles. The brackets indicate an unweighted average over all possible dipole orientations

$$\langle \ldots \rangle = \int \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} (\ldots),$$

where $d\Omega_i$ $(i = 1, 2)$ are differential elements of solid angle. The independent variable $z = \beta\mu_1\mu_2/r^3$ fixes the strength of interaction for a pair of dipoles with moments $\mu_1$ and $\mu_2$ separated by a displacement $\mathbf{r} = r\,\hat{\mathbf{r}}$ and interacting through the dipole–dipole tensor

$$\mathbf{T} = (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I})/r^3$$

where $\hat{\mathbf{r}}$ is a unit vector and $\mathbf{I}$ is the unit tensor. The dipoles are in contact with a thermal reservoir maintained at absolute temperature $T = (k\beta)^{-1}$, where $k$ is Boltzmann's constant, and $\beta$ is defined by this relation. In terms of $q$, the expressions

$(q - 1)$ and $-kT \ln q$ are, respectively, the angle-averaged $f$-function and the effective potential (cf. [3, 4], and references therein).

A Taylor series expansion of exp $(\beta \boldsymbol{\mu}_1 \,.\, \mathbf{T} \,.\, \boldsymbol{\mu}_2)$ about $z = 0$ is absolutely and uniformly convergent in the finite $z$-plane, and can therefore be integrated term-by-term, with the result

$$q(z) = \sum_{n=0}^{\infty} \frac{\langle \mathbf{n}_1 \,.\, \mathbf{T} \,.\, \mathbf{n}_2 \rangle^{2n}}{(2n)!} z^{2n},$$

where $\mathbf{n}_i = \boldsymbol{\mu}_i/\mu_i$ $(i = 1, 2)$ are unit vectors. The odd powers vanish on integration. Regarded as a function of the complex variable $z$, $q$ is real on the real axis; taken together with the dependence of $q$ on even powers of $z$, $q$ satisfies the symmetry relations $q^*(z) = q(z^*)$ and $q(-z) = q(z)$. The analytic continuation implied by the first symmetry relation is a consequence of Schwarz's reflection principle. Thus the values of $q$ in the sector $0 \leq \arg z \leq \pi/2$ determine $q$ in the entire complex plane.

If, as has been customary, the integrands in the Taylor coefficients are expressed in terms of trigonometric functions, expanded via the binomial theorem, and integrated term-by-term, known double series expansions for $q$ are obtained. If, instead, the vector and tensor properties of the integrand are used throughout the integration, it is possible to derive a very useful integral representation of the Taylor coefficients. To do this, one introduces temporarily the vector $\mathbf{u} = \mathbf{n}_1 \,.\, \mathbf{T}$; integrates, and noting that $r^6 \mathbf{T} \,.\, \mathbf{T} = 3\hat{\mathbf{r}}\hat{\mathbf{r}} + \mathbf{I}$, integrates again, with the result

$$\frac{\langle \mathbf{n}_1 \,.\, \mathbf{T} \,.\, \mathbf{n}_2 \rangle^{2n}}{(2n)!} = \frac{1}{(2n + 1)!} \int_0^1 (1 + 3x^2)^n \, dx.$$

The series for $q$ is easily summed using this integral representation. By substituting it into the series, invoking uniform convergence to interchange summation and integration, $q$ is reduced to the single quadrature

$$q(z) = \int_0^1 \frac{\sinh [z\sqrt{(1 + 3x^2)}]}{z\sqrt{(1 + 3x^2)}} \, dx$$

$$= \int_0^1 i_0[z\sqrt{(1 + 3x^2)}] \, dx$$

where $i_0$ is a modified spherical Bessel function of zero order. Both the integrand and its integral $q$ have Taylor-series expansions that converge throughout the finite $z$-plane and are therefore entire functions.

The Taylor coefficients $a_n = I_n/(2n + 1)!$ satisfy a recursion relation that facilitates their computation. The recursion relation for

$$I_n = \int_0^1 (1 + 3x^2)^n \, dx$$

is simpler than that of $a_n$. To find this relation, one integrates $I_n$ by parts, on the one hand, and expresses the integrand as

$$(1 + 3x^2)^n = (1 + 3x^2)^{n-1} + 3x^2(1 + 3x^2)^{n-1}$$

on the other. The integral

$$\int_0^1 x^2(1 + 3x^2)^{n-1} \, dx$$

is eliminated between the two expressions for $I_n$ to get the recursion relation

$$I_n = \frac{(2^{2n} + 2nI_{n-1})}{2n+1}, \qquad I_0 = 1.$$

$I_n$ satisfies a linear, first order, inhomogeneous difference equation whose solution is

$$I_n = \frac{2^{2n}(n!)^2}{(2n+1)!} \sum_{k=0}^{n} \binom{2k}{k}.$$

The corresponding recursion relation for $a_n$ is

$$a_n = \frac{1}{(2n+1)^2} \frac{a_{n-1} + 2^{2n}}{(2n)!}, \qquad a_0 = 1,$$

with solution

$$a_n = \left(\frac{2^n n!}{(2n+1)!}\right)^2 \sum_{k=0}^{n} \binom{2k}{k}.$$

The sum in the Taylor coefficients characteristic of previous formulations reappears in the solution of the recursion relation, though in a more symmetrical form, and with the sum now over central binomial coefficients. Direct use of the recursion relation avoids the need for explicit calculation of the sums in numerical computations. $I_n$ grows essentially geometrically as $n$ increases. Another recursion relation with the geometric growth removed can be constructed by explicitly factoring out $I_n$s asymptotic behaviour, further simplifying numerical computation.

The integrand of $I_n$ increases monotonically on the interval [0, 1]. For large $n$, most of the contribution to the integral comes from a small neighbourhood of $x = 1$. A straightforward application of Laplace's method [8] yields

$$I_n = \frac{2^{2n+1}}{3n} + O(n^{-2}), \qquad (n > 1),$$

as $n \to \infty$. Let $I_n = 2^{2n+1}b_n/3n$, then

$$q(z) = 1 + \frac{2}{3} \sum_{n=1}^{\infty} \frac{b_n(2z)^n}{n(2n+1)!}$$

and $b_n$ satisfies the recursion relation

$$2(2n+1)(n-1)b_n = 3n(n-1) + n^2 b_{n-1}, \qquad (n > 2), \qquad b_1 = 3/4,$$

$$b_n \to 1 \quad \text{as} \quad n \to \infty.$$

Using Stirling's approximation to the gamma function, the asymptotic form of $a_n$ can also be inferred from the asymptotic form of $I_n$; specifically,

$$a_n \sim \frac{e(e/n)^{2n+1}}{6n^{3/2}\sqrt{\pi}}.$$

Numerical computations show that the radius of convergence of $\ln q$ is about 2·4 [4]. The radius of convergence is determined by the presence of a simple pole (the nature and location of this singularity is set out in the next section) corresponding to the zero of $q$ nearest to $z = 0$. In fact, $q$ has an infinity of zeros, a result which can be inferred from the asymptotic behaviour of the Taylor coefficients. To show this, $q$ must first be classified with respect to the growth properties of its maximum modulus $M(R)$. The maximum modulus is the largest absolute value $q(z)$ assumes on a circle of radius $R$ about the origin. The existence of such a value for an entire function is guaranteed by standard theorems of complex analysis. An entire function whose maximum modulus satisfies

$$M(R) = \max_{R=|z|} |q(z)| = O[\exp(\sigma R^\rho)],$$

is said to be function of order $\rho$ and type $\sigma$, where $\rho$ and $\sigma$ are the greatest lower bounds for which the relation is true [9, 10]. That there are an infinite number of zeros can be inferred easily from the order of $q(\sqrt{s})$ where $s = z^2$. The order of $q(\sqrt{s})$ computed from its Taylor coefficients [10] is

$$\rho = -\lim_{n\to\infty} \sup\,(\ln n/\ln \sqrt[n]{|a_n|}) = 1/2.$$

According to Picard's first (little) theorem [10], fractional-order entire functions have an infinite number of zeros; therefore $q(\sqrt{s})$ has an infinite set of zeros, and $q(z)$ has a doubly infinite set of zeros. None of these zeros are real since $q(z)$ is positive for all real values of $z$. Moreover, in view of the symmetry relations, the zeros must occur in complex conjugate pairs. The order of $q(z)$ is twice that of $q(\sqrt{s})$; in this instance, one. The type of $q(\sqrt{s})$ (and of $q(z)$) may also be deduced from its Taylor coefficients [10] and is given by

$$\sigma = (1/e\rho) \lim_{n\to\infty} \sup\, n|a_n|^{\rho/n} = 2.$$

More precise results on the growth of $q(z)$ and on the distribution of zeros follow from an asymptotic analysis of $q$.

In addition to an integral representation and a series representation, the normalized partition function also has an infinite product representation. According to Hadamard's factorization theorem [9, 10], an order-one entire function with an infinite number of zeros has the representation

$$\begin{aligned} q(z) &= C \exp(Bz) \prod_{n=-\infty}^{\infty} \left(1 - \frac{z}{z_n}\right) \exp(-z/z_n) \\ &= C \exp(Bz) \prod_{n=1}^{\infty} \left(1 - \frac{z^2}{|z_n|^2}\right), \end{aligned}$$

where the $z_n$ are roots of $q$. The second equality is a consequence of the occurrence of the roots in complex conjugate pairs. Since $q(z)/\Pi[1 - (z/|z_n|)^2]$ is an even function that assumes the value one at $z = 0$, $B$ is necessarily zero and $C$ must equal one. The infinite product representation of $q$ assumes the simple form

$$q(z) = \prod_{n=1}^{\infty} \left(1 - \frac{z^2}{|z_n|^2}\right).$$

The genus of $q$, an additional classification of entire functions [9], follows immediately from its infinite product representation. The genus is the largest degree of the two polynomials $Bz$ and $z/z_n$ [9]; in this case, one.

The partition function and incomplete Bessel functions are easily connected through the differential equation

$$z\frac{d^2K}{dz^2} + \frac{dK}{dz} - zK = \sqrt{3} \cosh 2z,$$

satisfied by the integral

$$K(z) = \int_0^{\sinh^{-1}\sqrt{3}} \sinh(z \cosh t)\, dt,$$

which is itself proportional to $q$. The homogeneous part of the differential equation is satisfied by Macdonald and modified Bessel functions of zero order. The complete solution of the inhomogeneous equation can be found by variation of parameters. The particular integral satisfying this equation can be expressed in terms of Lipschitz–Hankel integrals [7, 11]. Such a solution obscures a natural generalization of Bessel functions which is brought out by seeking a contour-integral solution to the differential equation with one limit of integration defining a new independent variable. It is natural to regard these integrals as defining incomplete Bessel functions [7]. The contour-integral solution to the above differential equation is

$$\int_1^2 \frac{\sinh zt}{\sqrt{(t^2-1)}}\, dt,$$

which is identical, by an obvious change of variables, to $K(z)$.

Incomplete Bessel functions, with the exception of the twice-modified forms defined in the Appendix, have standard symbols defined by integral representations [7]. In terms of these symbols, including those defined in the Appendix, the normalized partition function takes the form

$$q(z) = -\frac{i\pi}{2z\sqrt{3}} L_0(i \sinh^{-1}\sqrt{3}, z) = \frac{\pi}{2z\sqrt{3}} M_0(\sinh^{-1}\sqrt{3}, z).$$

The first and second equality express $q$ in terms of once- and twice-modified incomplete Struve functions of zero order, respectively. The last form is preferable for the partition function since the complex unit $i$ is altogether absent when $z$ is real.

## 3. Asymptotic analysis

Integration by parts is the simplest method for generating the full asymptotic expansion of $q$ in the sector $|\arg z| \leq \pi/2 - \delta$. Unfortunately, the boundary terms tend to infinity at the lower limit of integration. This difficulty is easily overcome by splitting the partition function into two pieces $q = q_a + q_b$ where

$$q_a(z) = \frac{1}{z\sqrt{3}} \int_1^a \frac{\sinh zt}{\sqrt{(t^2-1)}}\, dt = O(\exp(az)/z^2)$$

and

$$q_b(z) = \frac{1}{z\sqrt{3}} \int_a^2 \frac{\sinh zt}{\sqrt{(t^2-1)}}\, dt.$$

The estimate for $q_a$ implied by the order relation is straightforward to verify by bounding the integral. On integrating $q_b$ by parts once, the remainder term is found to be $O(\exp(2z)/z^3)$ and $q_b = O(\exp(2z)/z^2)$. Therefore $q_a$ is seen to be subdominant with respect to $q_b$, and the entire asymptotic expansion of $q$ can be deduced from

$q_b$. Repeated integration by parts generates the full asymptotic expansion

$$q(z) \sim \frac{\exp(2z)}{6z^2} \sum_{n=0}^{\infty} \frac{n! P_n(2/\sqrt{3})}{(z\sqrt{3})^n}$$

$$= \frac{\exp(2z)}{6z^2}\left(1 + \frac{2}{3z} + \frac{1}{z^2} + \frac{22}{9z^3} + \frac{227}{27z^4} + \frac{1010}{27z^5} + \frac{5515}{27z^6} + \frac{107030}{81z^7} + \frac{800065}{81z^8} + \frac{20352290}{243z^9} + \dots\right), \quad |z| \to \infty.$$

Subdominant terms have been dropped, and the Legendre polynomials $P_n(2/\sqrt{3})$ appear via the identity

$$\frac{d^n}{dt^n}\left(\frac{1}{\sqrt{(t^2-1)}}\right)_{t=x} = \frac{(-)^n n!}{[\sqrt{(x^2-1)}]^{n+1}} P_n\left(\frac{x}{\sqrt{(x^2-1)}}\right),$$

which can be verified using the generating function for the Legendre polynomials. Tables 1 and 2 compare values of $q$ with their asymptotic approximations.

An asymptotic approximation for $\ln q(z)$,

$$\ln q(z) = 2z - 2\ln(z\sqrt{6}) + O(1/z), \qquad |z| \to \infty,$$

follows directly from the asymptotic expansion of $q$.

On the imaginary axis, $q_a$ is no longer subdominant. In fact, $q_a$ contains the leading contribution to the asymptotic expansion of $q$. The asymptotic expansion is best developed from the following integral representation of $q(iy)$

$$q(iy) = \frac{1}{y\sqrt{3}} \operatorname{Im} \int_0^{\sinh^{-1}\sqrt{3}} \exp(iy \cosh t)\, dt,$$

where $y = \operatorname{Im}(z)$. The integrand has saddle points at $n\pi$ where $n$ is any integer. The only relevant point is $n = 0$. However, no specific use of it is made here. The integral

Table 1. Optimal asymptotic approximation of the normalized partition function. Parentheses enclose base ten exponents.

| $z$ | Normalized partition function $q(z)$ | Optimal asymptotic approximation | Relative error |
|---|---|---|---|
| 1 | 1·37608 | 1·23151 | −1·05 (−1) |
| 2 | 3·17369 | 3·03323 | −4·43 (−2) |
| 4 | 3·95735 (1) | 3·93536 (1) | −5·56 (−3) |
| 6 | 8·75826 (2) | 8·75186 (2) | −7·30 (−4) |
| 8 | 2·56504 (4) | 2·56479 (4) | −9·81 (−5) |

Table 2. Ten-term asymptotic approximation of the normalized partition. Parentheses enclose base ten exponents.

| $z$ | Normalized partition function $q(z)$ | Ten-term asymptotic approximation | Relative error |
|---|---|---|---|
| 10 | 8·739921 (5) | 8·739805 (5) | −1·32 (−5) |
| 20 | 1·016284 (14) | 1·016784 (14) | −1·85 (−7) |
| 30 | 2·164392 (22) | 2·164392 (22) | −2·09 (−9) |
| 40 | 5·871522 (30) | 5·871522 (30) | −1·82 (−10) |
| 50 | 1·816727 (39) | 1·816727 (39) | −1·02 (−11) |

along $\Gamma_a$ can be expressed as the sum of integrals along the steepest-descent contours $\Gamma_b$ and $\Gamma_c$ (figure 1). The contour $\Gamma_b$ can be deformed into the contours $\Gamma_d$ and $\Gamma_e$. The integral along $\Gamma_e$ has no imaginary part and is therefore identically zero. The integral along $\Gamma_d$ is proportional to a well-known integral representation of the zero-order Bessel function $J_0(y)$ [12]. Thus $q(iy)$ has the alternate representation

$$q(iy) = \frac{\pi}{2y\sqrt{3}} J_0(y) - \frac{1}{y\sqrt{3}} \operatorname{Im} i \exp(2iy) \int_0^\infty \frac{\exp(-yu)}{\sqrt{[-(u^2/3) + (4iu/3) + 1]}} \, dt.$$

The integral on the right-hand side is a Laplace integral satisfying the conditions of Watson's lemma [8]. Its full asymptotic expansion can be obtained immediately by integrating the exponential times the Taylor series expansion of the non-exponential part of the integrand. Since the asymptotic expansion of $J_0(y)$ is well known [8, 12], the full asymptotic expansion of $q(iy)$ follows:

$$q(iy) = \sqrt{(1/6\pi y^3)}[a(y) \cos(y - \pi/4) + b(y) \sin(y - \pi/4)] + (1/3y^2)[c(y) \cos 2y + d(y) \sin 2y],$$

where

$$a(y) \sim \sum_{n=0}^{\infty} \frac{(-)^n [\Gamma(2n + \frac{1}{2})]^2}{(2n)!(2y)^{2n}}, \quad y \to \infty,$$

$$b(y) \sim \sum_{n=0}^{\infty} \frac{(-)^{n+1} [\Gamma(2n + \frac{3}{2})]^2}{(2n+1)!(2y)^{2n+1}}, \quad y \to \infty,$$

$$c(y) \sim \sum_{n=0}^{\infty} \frac{(-)^{n+1}(2n)! P_{2n}(2/\sqrt{3})}{(y\sqrt{3})^{2n}}, \quad y \to \infty,$$

and

$$d(y) \sim \sum_{n=0}^{\infty} \frac{(-)^{n+1}(2n+1)! P_{2n+1}(2/\sqrt{3})}{(y\sqrt{3})^{2n+1}}, \quad y \to \infty.$$

It is evident from this asymptotic expansion that $q$ has roots on the imaginary axis approximately determined by the roots of $\cos(y - \pi/4)$. These roots are given to

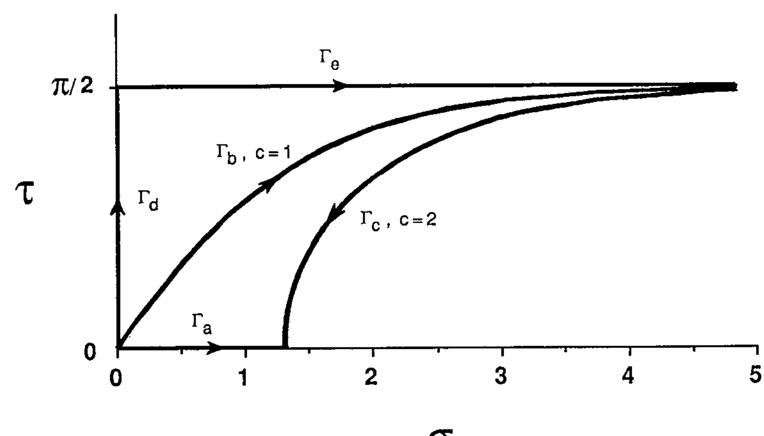


Figure 1. $\Gamma_a$ and $\Gamma_b$ are constant phase contours of $\exp(iy \cosh t)$ plotted in the complex $(t = \sigma + i\tau)$-plane. Constant phase contours satisfy $\cosh(\sigma) \cos(\tau) = c$ $(c = 1, 2)$.

Table 3. Leading asymptotic approximation of the first five zeros of the normalized partition function on the positive imaginary axis. Parentheses enclose base ten exponents.

| Zeros | Leading asymptotic approximation | Relative error |
|---|---|---|
| 2·426659 | 2·356194 | −2·90 (−2) |
| 5·498779 | 5·497787 | −1·80 (−4) |
| 8·659151 | 8·639380 | −2·28 (−3) |
| 1·178528 (1) | 1·178097 (1) | −3·66 (−4) |
| 1·493355 (1) | 1·492257 (1) | −7·36 (−4) |

leading order by

$$z_n \sim \pm i\left(\frac{4n+3}{4}\right)\pi, \qquad n \to \infty.$$

Table 3 compares the first five roots of $q$ on the positive imaginary axis with their leading asymptotic approximations. The magnitude of the zero closest to the origin agrees to two significant figures with the radius of convergence reported elsewhere from a numerical analysis of the effective potential's Maclaurin series [4]. It is also evident that the imaginary roots of $q$ correspond to simple poles of the effective potential.

Since $q$ is proportional to an incomplete Struve function, and incomplete Struve functions can be expressed as a linear combination of incomplete Hankel functions, an alternate derivation of the foregoing asymptotic expansions is possible starting from asymptotic expansions of incomplete Hankel functions [7].

## 4. Polynomial approximations

For practical applications, it is convenient to have accurate computationally-efficient approximations for the orientation partition function and the effective potential for all real values of $z$. The polynomial approximations that follow are curve-fits to values of $q(x)$ or $6x^2 \exp(-2x)q(x)$ computed from a Taylor series representation of $q$ with $x = \mathrm{Re}\,(z)$. Approximations to the effective potential follow directly from $\ln q(x)$.

Polynomials of degree $N$ are fit to $N + 1$ equally spaced points for the independent variable appropriate to each interval. The degree of the polynomials, number of polynomials, and the length of the intervals have been chosen so that accuracy and computational effort for each interval are approximately the same, and so that the coefficients of the polynomials have, insofar as is possible, integer parts of modest and comparable size. Bounds on the relative error $\varepsilon$ are given for each interval.

On the interval $0 \leqslant x \leqslant 3{\cdot}4$; $t = (x/4)^2$,

$$q(x) = 1 + 5{\cdot}333333t + 10{\cdot}24t^2 + 10{\cdot}77406t^3 + 7{\cdot}26529t^4 + 3{\cdot}405843t^5 + 1{\cdot}17305t^6 + 0{\cdot}301138t^7 + 0{\cdot}076646t^8,$$

and $|\varepsilon| < 7{\cdot}4 \times 10^{-6}$.

On the interval $3{\cdot}4 \leqslant x \leqslant 5{\cdot}4$; $t = (x - 3{\cdot}4)/2$,

$$q(x) = 17{\cdot}116 + 46{\cdot}204t + 68{\cdot}098t^2 + 71{\cdot}055t^3 + 52{\cdot}163t^4 + 50{\cdot}538t^5 - 6{\cdot}467t^6 + 44{\cdot}03t^7 - 20{\cdot}446t^8 + 10{\cdot}593t^9,$$

and $|\varepsilon| < 4{\cdot}4 \times 10^{-6}$.

On the interval $5{\cdot}4 < x < \infty$; $t = 4/x$,

$$6x^2\,e^{-2x}q(x) = 1 + 0{\cdot}167707t + 0{\cdot}026766t^2 + 0{\cdot}47681t^3 - 2{\cdot}48106t^4 + 7{\cdot}315849t^5 - 10{\cdot}43147t^6 + 7{\cdot}020614t^7 - 1{\cdot}82078t^8,$$

and $|\varepsilon| < 9{\cdot}7 \times 10^{-6}$.

## 5. Conclusion

The dipole–dipole effective potential for permanent dipoles is the analogue of the London dispersion potential for induced dipoles. Both potentials have their origins in multipole expansions of charge distributions truncated at the dipole term, and both result from averages over fluctuations—thermal in the former case, and quantum in the latter. The London dispersion potential is best known for providing the theoretical justification for the functional form of the attractive component of the Lennard-Jones potential. Because of its simple form, it can be represented as proportional to the elementary analytic function $1/r^6$. Although the dipole–dipole potential for permanent dipoles is arguably the simplest and most important example of an anisotropic potential, no corresponding analytic function has been known for its effective potential. That gap has been filled here by integrating the orientation partition function in terms of a twice-modified incomplete Struve function of zero order.

More important aspects of this analysis, however, are the accompanying computational approximation and analytic characterization of the orientation partition function and the effective potential. The polynomial approximations and their logarithms in § 4, for example, require about the same computational effort as standard algorithms for computing low order Bessel functions, and the asymptotic approximations in § 3 completely characterize the classical low-temperature behavior of the partition function and the effective potential.

Analytic and asymptotic properties of the partition function reveal similarities and differences with other simple partition functions familiar from statistical mechanical treatments of dipoles. Knowledge of the shared analytic properties of these functions can be useful for setting up approximations, especially if the approximations are *ad hoc* in character, or if a variational approximation is needed that retains some of the analytic and asymptotic character of dipolar systems.

Three functions that can usefully be compared with the dipole–dipole orientation partition function are the partition functions for, respectively, (1) an Ising dipole pair, (2) a dipole in an external field, and (3) the Boltzmann factor for the attractive component of the Lennard-Jones effective potential from dipolar thermodynamic perturbation theory [3]. With the exception of the Lennard-Jones effective potential, these functions represent distinct physical systems, and only qualitative comparisons to the orientation partition function are possible.

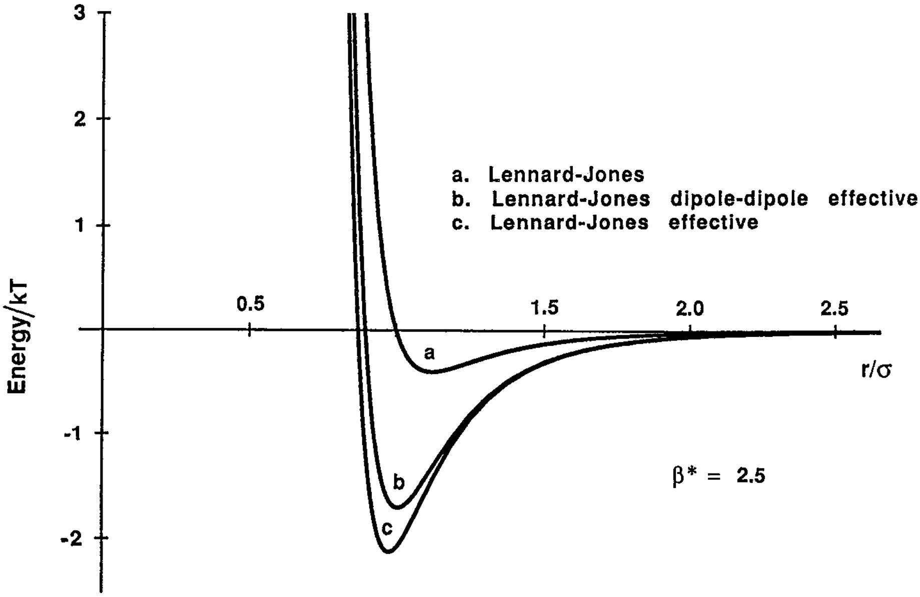


Figure 2. Lennard-Jones, Lennard-Jones dipole–dipole effective, and Lennard-Jones effective potentials shown at $T = 298\,\mathrm{K}$ with $\beta^* = \beta\mu^2/\sigma^3 = 2{\cdot}5$ and with the Lennard-Jones parameters $\varepsilon/k = 119{\cdot}8\,\mathrm{K}$ and $\sigma = 3{\cdot}405\,\text{Å}$ (argon–argon pair potential).

The partition function for an Ising dipole pair is proportional to a hyperbolic cosine, cosh $(\beta J)$, where $J$ is the coupling constant for a pair of dipoles. The partition function for an arbitrarily orientable point dipole in an external field is proportional to a modified spherical Bessel function of zero order, $i_0(\beta\mu E)$, where $E$ is an external electric field. Like the orientation partition function of this paper, both of these functions are genus one, order one, entire functions of the independent variable $\beta$, and both possess an infinite number of zeros along the imaginary axis. The low temperature behaviors (leading asymptotic approximations) of the Ising dipole pair, dipole-external field, and dipole–dipole partition functions are proportional to $\exp(\beta J)$, $\exp(\beta\mu E)/\beta\mu E$, and $\exp(2\beta\mu^2/r^3)/(\beta^2\mu^4/r^6)$, respectively. While the denominators of these three functions differ by factors of $\beta$, $\beta$ appears in the numerators as an exponent, and the exponents are all linear functions of $\beta$. It is the exponentials in the numerators that dominate the low temperature behaviour. Thus, although these functions represent entirely different physical situations, they share qualitatively similar analytic properties.

The Boltzmann factor for the attractive component of the Lennard-Jones effective potential, $\exp[4\beta\varepsilon(\sigma/r)^6 + \beta^2\mu^4/3r^6]$, where $\varepsilon$ and $\sigma$ are energy and length parameters, respectively, contrasts sharply with the partition functions described above. Regarded as a function of $\beta$, the Boltzmann factor is a genus two, order two, entire function, with no zeros whatsoever. Although, for interactions between permanent dipoles, it correctly reproduces the leading high-temperature behaviour, its quadratic dependence on $\beta$ results in strong departures from the correct classical low-temperature behaviour. These departures also appear for increasing dipole moment and decreasing internuclear separation. Their effect is best displayed in the potentials rather than in the partition functions.

Figure 2 depicts (*a*) the Lennard-Jones potential, $U_{LJ} = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, (*b*) the Lennard-Jones dipole–dipole effective potential, $U_{LJ} - \beta^{-1} \ln q(z)$, and (*c*) the Lennard-Jones effective potential, $U_{LJ} - z^2/3\beta$. For $\beta^* = \beta\mu^2/\sigma^3 = 2{\cdot}5$, it is clear that the Lennard-Jones effective potential substantially overestimates the well depth of the full potential, and shifts the steeply repulsive part of the potential to smaller values of the internuclear separation. These departures from the actual Lennard-Jones dipole–dipole effective potential are, as for the Boltzmann factor, a consequence of the strong quadratic growth of the term $z^2/3$, compared to the linear growth of the dipole–dipole effective potential term, $\ln q(z) = O(z)$, as $z \to \infty$. The dependence of the term $z^2/3\beta$ in the Lennard-Jones effective potential on the inverse sixth power of the internuclear separation, $(\sigma/r)^6$, makes it a useful approximation for corresponding state calculations. However, in the dipole–dipole effective potential, this dependence softens, for decreasing internuclear distances, to $(\sigma/r)^3$.

The error generated by a substitution of $z^2/3\beta$ for the full dipole–dipole effective potential increases dramatically for increasing $\beta^*$, as is evident in figure 3. In this figure, the dimensionless difference, $-z^2/3 + \ln q$, between the approximate and the true dipole–dipole effective potential is plotted for values of $\beta^*$ ranging from 1 to 4. These values are typical of those that occur in studies of dipolar systems (cf. [4] and [13]). For $\beta^* = 1$, the Lennard-Jones effective potential and the Lennard-Jones dipole–dipole effective potential are indistinquishable if plotted to the scale shown in figure 2. However, as figure 3 illustrates, for $\beta^* = 4$, (the critical point $\beta^*$ for hard-sphere dipolar systems [13]), departures from $z^2/3$ when $r/\sigma = 1$ are substantial.

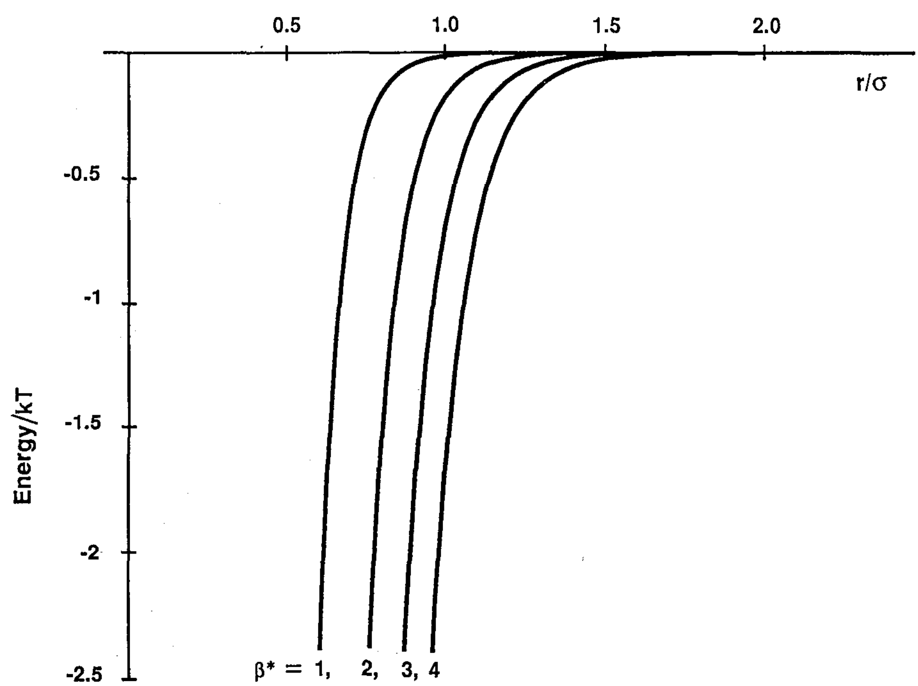


Figure 3. The difference, $-z^2/3 + \ln q(z)$, between the aproximate and full dipole–dipole effective potential for values of $\beta^* = \beta\mu^2/\sigma^3$ ranging from 1 to 4.

In addition to its qualitative analytic similarities to $q$, the partition function for a dipole in an external field permits a physical interpretation of the dipole–dipole orientation partition function's integral representation,

$$Q(z) = (4\pi)^2 \int_0^1 i_0[z\sqrt{(1 + 3x^2)}]\, dx.$$

If an orientation dependent field is defined by $E(x) = \mu\sqrt{(1 + 3x^2)}/r^3$, then $Q$ assumes the form,

$$Q(z) = (4\pi)^2 \int_0^1 i_0[\beta\mu E(x)]\, dx.$$

Except for its $x$ dependence, the functional form of the integrand is identical to that of a partition function of a single dipole in an external field. Thus, the orientation function could be viewed as the partition function of a dipole in its own induced external field, averaged over all possible orientations inducing that field. The second of the two dipoles in the pair acts as the polarized 'medium' generating the induced field.

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## Appendix

The integral representations

$$I_\nu(w, z) = \frac{2z^\nu}{A_\nu} \int_0^w \cosh(z \cos t) \sin^{2\nu} t\, dt$$

and

$$L_\nu(w, z) = \frac{2z^\nu}{A_\nu} \int_0^w \sinh(z \cos t) \sin^{2\nu} t\, dt$$

with $A_\nu = 2^\nu\Gamma(\nu + 1/2)\Gamma(1/2)$ represent modified incomplete Bessel and Struve functions throughout the complex plane [7]. They are related to the incomplete Bessel and Struve functions by the identities

$$I_\nu(w, z) = \exp(-i\nu\pi/2) J_\nu(w, iz)$$

and

$$L_\nu(w, z) = -i \exp(-i\nu\pi/2) H_\nu(w, iz).$$

The twice-modified incomplete Bessel and Struve functions, $G$ and $M$ respectively, are defined here by the replacement $w \to iw$ in the foregoing integral representations. They are related to the modified functions by the identities

$$G_\nu(w, z) = -i \exp(-i\nu\pi) I_\nu(iw, z)$$

and

$$M_\nu(w, z) = -i \exp(-i\nu\pi) L_\nu(iw, z).$$

$G$ and $M$ were chosen because they are the two letters in the alphabetic sequence $G-N$ that are not used to represent Bessel functions. With the exception of $Y$, the commonly used letters for Bessel functions are contained in this interval. The most likely conflict with other special functions is with Kummer's confluent hypergeometric function $M$, since this function is proportional to Bessel functions for some choices of its parameters. If the two types of functions must be used concurrently, ${}_1F_1$ is a standard alternate choice for the confluent hypergeometric function.

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