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A closed form for the second virial coefficient of the Lennard–Jones gas

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Abstract. The Lennard–Jones interatomic potential for spherically symmetric particles is given by $U(r) = M/r^m - N/r^n$, where r is the separation of the centres of the particles, and M and N are positive constants. The classical second virial coefficient for such a gas will be evaluated in closed form for the case $m = 2n$, in terms of the parabolic cylinder functions. To leading order, dipole–dipole interactions give $n = 6$, so these results are applicable to the case $m = 12$, which is fortuitously close to the best empirical value.

The Lennard–Jones interatomic potential for spherically symmetric particles is given by

$$U(r) = M/r^m - N/r^n, \tag{1}$$

where r is the separation of the centres of the particles, and M and N are positive constants.

The classical second virial coefficient for spherically symmetric particles is

$$B_2 = 2\pi \int_0^\infty [1 - \exp(-\beta U)] r^2 \, dr, \tag{2}$$

where $\beta = (kT)^{-1}$ (see, for example, Mayer and Mayer (1940)), and can be evaluated as an infinite series for the general Lennard–Jones potential (Jones 1924). However, for the case $m = 2n$ we can make the substitutions

$$x = \beta N r^{-n}, \qquad \omega = (\beta N^2/2M)^{1/2}, \qquad B_2' = (2\pi)^{-1}(2M/N)^{-3/n} B_2 \tag{3}$$

and obtain the expression

$$B_2' = \frac{\omega^{6/n}}{n} \int_0^\infty \left[1 - \exp\left(x - \frac{x^2}{2\omega^2}\right)\right] x^{-1-3/n} \, dx. \tag{4}$$

It can be seen this expression depends only on the parameter ω. Integrating by parts, this becomes

$$B_2' = \frac{\omega^{6/n}}{n}\left[-\frac{n}{3} x^{-3/n}\left(1 - \exp\left(x - \frac{x^2}{2\omega^2}\right)\right)\right]_0^\infty + \frac{\omega^{6/n}}{3} \int_0^\infty x^{-3/n}\left(\frac{x}{\omega^2 - 1}\right) \exp\left(x - \frac{x^2}{2\omega^2}\right) dx. \tag{5}$$

The first term vanishes at $x = \infty$, and also at $x = 0$ (corresponding to $r = \infty$) provided $n > 3$; this is in fact a necessary condition for existence of the virial. Thus we can write

$$B_2' = \tfrac{1}{3}\omega^{6/n}(\omega^{-2} I(\omega, 2 - 3/n) - I(\omega, 1 - 3/n)), \tag{6}$$

where

$$I(\omega, \tau) = \int_0^\infty x^{(\tau-1)} \exp\left(x - \frac{x^2}{2\omega^2}\right) dx. \tag{7}$$

The Lennard–Jones method effectively consisted of expanding the e^x term; however we note this is a standard integral for the parabolic cylinder functions $D_{-\tau}$:

$$I(\omega, \tau) = \Gamma(\tau)\omega^\tau \exp(\omega^2/4) D_{-\tau}(-\omega) \tag{8}$$

(Gradshteyn and Ryzhik 1965) with normalisation given in the same reference. They are tabulated in, for example, Abramowitz and Stegun (1965) (but none of the further references in this book tabulate the relevant type of function). Thus, using elementary properties of the Γ function,

$$B_2' = \tfrac{1}{3}\Gamma(1-3/n)\omega^{3/n} \exp(\omega^2/4)[(1-3/n)D_{-2+3/n}(-\omega) - \omega D_{-1+3/n}(-\omega)]. \tag{9}$$

Explicitly, for the case $n = 6$, $m = 12$, to which the remainder of this work pertains, the second virial coefficient B_2 is given by

$$B_2 = (\pi^{3/2}/3)(2M/N)^{1/2}\omega^{1/2} \exp(\omega^2/4)(D_{-3/2}(-\omega) - 2\omega D_{-1/2}(-\omega)). \tag{10}$$

The behaviour of this expression has been extensively studied as a function of temperature in reduced variables (Barker *et al* 1966, Bird *et al* 1954), although not in closed form. At low temperatures, we use the standard large-argument expansions of the parabolic cylinder functions (Abramowitz and Stegun 1965) to show that

$$B_2 \approx -(2^{1/2}\pi^{3/2}/3)(2M/N)^{1/2}\omega^{-1} \exp(\omega^2/2). \tag{11}$$

The dominant term acts as $\exp(|U_{\min}|/kT)$, which is as expected from the method of steepest descents. At high temperatures, the small-argument expansions yield

$$B_2 \approx (2\pi/3)\Gamma(\tfrac{3}{4})(M/kT)^{1/4}[1 - (\Gamma(\tfrac{1}{4})^2/4\pi)\omega \ldots], \tag{12}$$

where the leading term has been written out in full in order to exhibit clearly its independence of N. This is because the collisions are sufficiently energetic so as not to 'see' the weak attractive term. However collisions at very high energies can no longer be represented by a simple power law of repulsion, so this expression is not to be taken too seriously. In practice the virial coefficient levels off to a constant value; this corresponds to an impenetrable atomic core. Evidently no atom is truly impenetrable, but all would long since have ionised at energies sufficient to perturb this core. Finally, the Boyle temperature T_B is that temperature at which $B_2 = 0$, and is calculable from $\omega_B = 0{\cdot}764\,950\,8674\ldots$.

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