3.2.x Sutherland Potential

The general form of the interaction between atoms or molecules comprises a repulsive part at short distances and an attractive part at large distances. The Lennard-Jones 6-12 potential is often used as an analytical representation of the interaction. The attractive tail, a consequence of fluctuation-induced electric dipole moments, is well-described by the r^{-6} law. However the r^{-12} description of the repulsive core is but a simple power law approximation to the actual close-range interaction. The popularity of the 6-12 potential lies principally in its mathematical elegance.

The Sutherland potential treats the short-distance repulsion in a different way; it approximates the interaction as a hard core. The attractive tail is described by the conventional dipolar r^{-6} law. However it is instructive – and possible – to consider a generalisation of this model whereby the long-range attraction is described by a general power r^{-m} law.
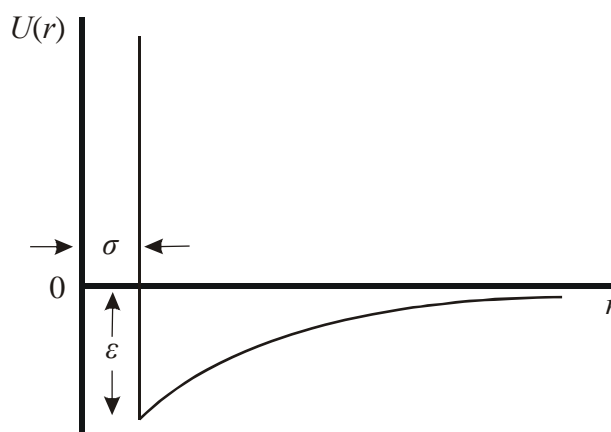

Fig. 3.x *Sutherland potential*

The form of the Sutherland potential is shown in Fig. 3.x. The generalised Sutherland potential, incorporating the parameter m is given by

$$U(r) = \infty \qquad r < \sigma$$

$$= -\varepsilon\left(\frac{\sigma}{r}\right)^m \qquad r > \sigma.$$

As with the Lennard-Jones potential, this potential has a universal form, scaled with an energy parameter ε and a distance parameter σ.

The second virial coefficient is given by

$$B_2(T) = -2\pi \int_0^\infty r^2 \left(e^{-U(r)/kT} - 1\right) dr$$

so using the mathematical form for $U(r)$, the integral splits into two parts

$$B_2(T) = 2\pi \int_0^\sigma r^2 \, \mathrm{d}r - 2\pi \int_\sigma^\infty r^2 \left(e^{\frac{\varepsilon}{kT}\left(\frac{\sigma}{r}\right)^m} - 1 \right) \mathrm{d}r$$

$$= \frac{2}{3}\pi\sigma^3 - 2\pi \int_\sigma^\infty r^2 \left(e^{\frac{\varepsilon}{kT}\left(\frac{\sigma}{r}\right)^m} - 1 \right) \mathrm{d}r .$$

We substitute $x = r/\sigma$ and $\tau = kT/\varepsilon$, so that

$$B_2(\tau) = \frac{2}{3}\pi\sigma^3 \left\{ 1 - 3 \int_1^\infty x^2 \left(e^{1/\tau x^m} - 1 \right) \mathrm{d}x \right\}.$$

We may evaluate the integral as a series in $1/\tau$ by expanding the exponential and integrating term by term. This gives

$$B_2(\tau) = \frac{2}{3}\pi\sigma^3 \left\{ 1 - 3 \sum_{n=1}^\infty \frac{\tau^{-n}}{n!(mn-3)} \right\}$$

but the leading 1 in the bracket may be subsumed as the $n = 0$ term of the sum:

$$B_2(\tau) = -2\pi\sigma^3 \sum_{n=0}^\infty \frac{\tau^{-n}}{n!(mn-3)}$$

$$= \frac{2}{3}\pi\sigma^3 \left(1 - \frac{3}{(m-3)\tau} - \frac{3}{2(2m-3)\tau^2} - \frac{1}{6(m-1)\tau^3} - \frac{1}{8(4m-3)\tau^4} - \cdots \right).$$

For the special case of the Sutherland potential we have $m = 6$, so that

$$B_2(\tau) = -\frac{2}{3}\pi\sigma^3 \sum_{n=0}^\infty \frac{\tau^{-n}}{n!(2n-1)}$$

$$= \frac{2}{3}\pi\sigma^3 \left(1 - \frac{1}{\tau} - \frac{1}{6\tau^2} - \frac{1}{30\tau^3} - \frac{1}{168\tau^4} - \cdots \right).$$

However, in this case it is possible to express $B_2(\tau)$ in terms of the imaginary error function Erfi, as

$$B_2(\tau) = \frac{2}{3}\pi\sigma^3 \left(e^{1/\tau} - \sqrt{\frac{\pi}{\tau}} \, \mathrm{Erfi} \frac{1}{\sqrt{\tau}} \right).$$

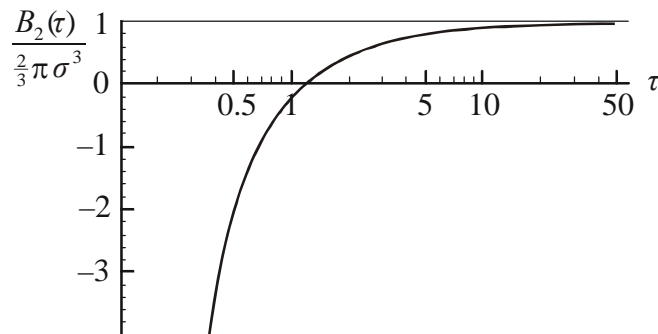This is plotted in Fig. 3.y below.

Fig. 3.y *Second virial coefficient for the Sutherland potential*

The Boyle temperature and the inversion temperature for this gas may be found from their definitions

$$B_2(T) = 0 \quad \rightarrow \quad T_{\mathrm{B}}$$

$$\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} - \frac{B_2(T)}{T} = 0 \quad \rightarrow \quad T_{\mathrm{i}}$$

to give

$$T_{\mathrm{B}} = 1.171\, \varepsilon/k$$
$$T_{\mathrm{i}} = 2.215\, \varepsilon/k \,.$$

The tangent construction for the inversion temperature (Section 3.3.4 and Fig. 3.8) is shown in Fig. 3.z.

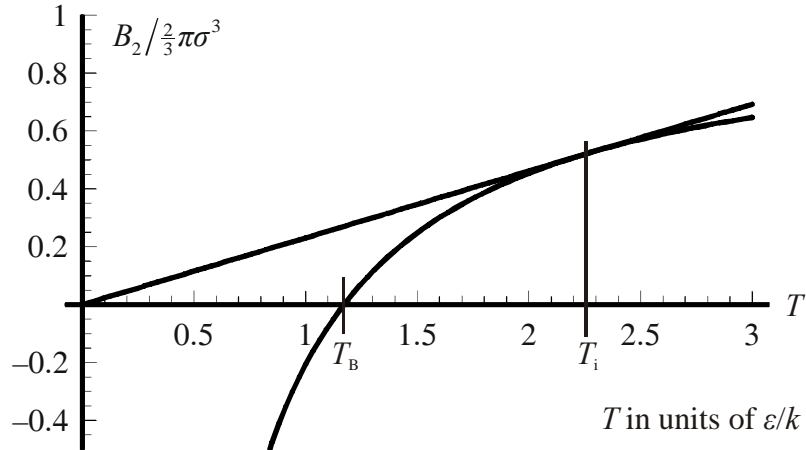Fig. 3.z *Boyle temperature and inversion temperature*

The ratio is then

$$T_{\mathrm{i}}/T_{\mathrm{B}} = 1.259 \,.$$

The interesting point about the Sutherland potential is that it gives the high-temperature behaviour of the $B_2(T)$ as

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3 \left(1 - \frac{\varepsilon}{kT} - \dots \right) ;$$

the limiting value at high temperatures is the hard core $2\pi\sigma^3/3$, while the leading deviation goes as T^{-1}.

[Compare with square well potential:

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3 \left(1 - \frac{\left(R^3 - 1\right)\varepsilon}{kT} - \dots \right).$$

Again the limiting high temperature value is the hard core expression and the leading deviation goes as T^{-1}. Note R is dimensionless, greater than unity. And ε is different in the two cases, i.e.

$$\varepsilon_{\mathrm{S}} = \left(R^3 - 1\right)\varepsilon_{\mathrm{sw}} \,.$$]

By contrast, the second virial coefficient for the Lennard-Jones gas does not have such a simple high-temperature behaviour – a consequence of the 'softness' of the hard core. In the high temperature limit

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3\left(-\frac{1}{2}\Gamma\left(-\frac{1}{4}\right)\left(\frac{\varepsilon}{kT}\right)^{1/4}\right)$$

$$\sim \frac{2}{3}\pi\sigma^3\left(2.45\left(\frac{\varepsilon}{kT}\right)^{1/4}\right),$$

so that in this case $B_2(T) \to 0$ as $T \to \infty$; the second virial coefficient tends to zero rather than the hard core limiting value.

D. Levi and M. de Llano, *Closed form of second virial coefficient for Sutherland potential*, J. Chem. Phys. 63, 4561-4562 (1975).

J. Tian and Y. Gui, *Modification to the Van der Waals Equation of State*, J. phase equilib, 24, 533-541 (2003).