

10.40 Thermodynamics

Fall 2003

Exam 2

Problem 4

4. (20 points) For a fluid whose intermolecular interactions follow the Sutherland potential described in Problem Set 8 (Problem 10.12 of the text):

- (a) (10 points) Can $B(T)$, the second virial coefficient, be positive or negative or zero? Justify your answer and explain its significance in terms of molecular interactions.
- (b) (10 points) Do you expect that this fluid will exhibit a Zeno point condition at high density ($\rho \gg 0$) where the compressibility factor $Z = PV/RT$ equals unity? Explain the rationale behind your answer.

Solution:

(a)

The Sutherland potential combines hard sphere repulsion with Lennard-Jones $1/r^6$ attraction to give:

$$\Phi_{ij}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ -\varepsilon(\sigma/r)^6 & \text{for } r > \sigma \end{cases}$$

As we saw in Problem 10.12, it can be shown that the Sutherland potential results in the van der Waals equation of state when pairwise additivity is assumed and $|\Phi_{ij}|$ is calculated from the Sutherland potential.

The 2nd virial coefficient, $B(T)$, also only depends on binary interactions between molecules. Therefore, the virial EOS should be identical to the van der Waals EOS in the low density limit, where

$$\text{vdW: } P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V} + (RTb - a) \frac{1}{V^2} + \dots$$

$$\text{virial: } P = \frac{RT}{V} + B(T) \frac{RT}{V^2} + \dots$$

Note that the equations of state have been truncated after the V^3 term. The expansion and truncation of the denominator of the first term of the vdW EOS was demonstrated in Problem Set 5, Problem 3. In this problem as well numerous times in class, we have seen that the term $(RTb - a)$ can be positive, negative, or zero. Therefore, $B(T)$ can also be positive, negative, or zero, depending on the value of T for a given V . Moreover, the significance of the value of $B(T)$ in terms of the molecular interactions is analogous to the interpretation of the value of $(RTb - a)$:

If $B(T)$ is ... $\left\{ \begin{array}{l} (+) \text{ repulsive molecular forces dominate} \\ 0 \text{ attractive and repulsive terms are equal (Zeno Pt.)} \\ (-) \text{ attractive molecular forces dominate} \end{array} \right.$

Alternatively, $B(T)$, can be calculated from the Sutherland potential. From Equation (10-114):

$$B(T) = -2\pi N_A \int_0^\infty [e^{-\beta\Phi(r)} - 1] r^2 dr \quad (10-114)$$

For $r < \sigma$, where a hard sphere repulsion is assumed:

$$-2\pi N_A \int_0^\sigma [e^{-\beta\infty} - 1] r^2 dr = -2\pi N_A \int_0^\sigma [0 - 1] r^2 dr = \frac{2\pi N_A \sigma^3}{3}$$

For $r > \sigma$, where a Lennard-Jones $1/r^6$ attraction is assumed:

$$-2\pi N_A \int_\sigma^\infty [e^{\beta\epsilon(\sigma/r)^6} - 1] r^2 dr = \begin{cases} -\infty & \text{as } T \rightarrow 0 \text{ (} \beta \rightarrow \infty \text{)} \\ 0 & \text{as } T \rightarrow \infty \text{ (} \beta \rightarrow 0 \text{)} \end{cases}$$

Summing the contributions, we have

$$B(T) = \frac{2\pi N_A \sigma^3}{3} + f(T) \text{ where } f(T) \text{ ranges from } 0 \text{ to } -\infty$$

The key to solving this problem using the Sutherland potential was realizing that the hard sphere interaction contributed a positive term to $B(T)$, while the LJ attractive term contributed a negative term. The hardest step was showing that the integral for the LJ attractive term was indeed always negative. Some students showed this as done above. Others expanded the integral by expanding the exponential as a power series and showing that each term was negative. Others noted in words the sign of each contribution. Any of these methods was acceptable.

Once again, we see that $B(T)$ can be positive, zero, or negative, depending on the value of T . From this development, it is even easier to see that repulsive (hard sphere) forces dominate for positive values of $B(T)$, while attractive (LJ) forces dominate for negative values of $B(T)$. It is also clear that these forces are equally balanced when $B(T) = 0$.

(b)

We can no longer use the truncated version of either the virial equation of state or van der Waals EOS that we developed in part (a) because they only apply at lower densities, whereas we are now dealing with densities much greater than zero. (Therefore, saying that $B(T) = 0$ gives the Zeno Point condition is not correct, since this gives the trivial solution that $Z = 1$ for an ideal gas at the Boyle point.) However, if we keep our pairwise additivity assumption, we can still derive the van der Waals EOS from the Sutherland potential as we did in Problem 10.15, so that:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

still applies. Although the Sutherland potential only assumes pairwise additivity, the vdW EOS is still able to account for tertiary, quaternary, etc. interactions by approximating a tertiary interaction as 3 binary interactions, etc. In the end, the a term accounts for and corrects for all of these attractive interactions, while the b term accounts for the hard-sphere repulsion.

From the vdW EOS, we clearly see the interaction of attractive and repulsive forces. We can conclude that at any given density, there will always be a point where the repulsive forces and attractive forces balance each other, resulting in the case where it *appears* that there is no interaction potential between the molecules, resulting in a Zeno Point condition.

We could also come to the same conclusion by looking at the virial form of the vdW EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \approx \frac{RT}{V} + B \frac{RT}{V^2} + C \frac{RT}{V^3} + \dots$$

This is similar to the virial EOS. We must realize that in order for this form of the equation to be accurate at high densities, a large number of terms are necessary. These terms will cancel each other out at the Zeno Point condition. Since this interaction potential has both attractive and repulsive terms, there must be some point where these forces balance each other out.