

Intermolecular Potentials and The Second Virial Coefficient

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Goal

This worksheet explores the relationship between the second virial coefficient and the intermolecular potential. Students examine and adjust parameters associated with the hard-sphere, square-well, and Lennard-Jones potentials. They subsequently use these potentials to compute the second virial coefficient for several substances, exploring its temperature dependence and developing an understanding of its relationship to the compression factor and intrinsic molecular properties.

Prerequisites

Prior to beginning this exercise students should have a rudimentary understanding of

- differential and integral calculus
- basic MathCad operations
- the ideal gas law and the virial equation of state
- the qualitative nature of intermolecular interactions

Objectives

Upon completion of this exercise, students will have

- examined graphically the hard-sphere, square-well, and Lennard-Jones intermolecular (IM) potentials
- adjusted IM parameters and discussed corresponding changes in each potential
- used the hard-sphere, square-well, and Lennard-Jones potentials to compute values of the second virial coefficient (B)
- graphed the temperature dependence of B for the square-well and Lennard-Jones potentials
- discussed the significance of this temperature dependence relative to attractive and repulsive interactions
- computed B for different particle systems and discussed differences in terms of molecular properties
- discussed differences between IM potentials and noted the relevance of each to real molecular properties
- used computed values of B to explore the temperature dependence of the compression factor Z for the square-well and Lennard-Jones potentials

General Notes

Text and regions designated as instructor's notes are set in bold and highlighted in gray; these regions do not appear in the student version of this document. Solutions to selected problems are also presented and highlighted in gray.

Student exercises are highlighted in teal.

General comments, instructions, and equation labels are highlighted in blue.

Note that MathCad units have been disabled to facilitate some of the derivations and computations.

References

1. Reid, B. P. *J. Chem. Educ.* **1996**, 73, 612-615.
2. Atkins, P. W.; de Paula, J. *Physical Chemistry*, 7th Edition; W.H. Freeman & Company: New York, 2002; pp 671-672, 705-706.
3. McQuarrie, D. A.; Simon J. D. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, 1997; pp 658-665.
4. Noggle, J. H. *Physical Chemistry*, 2nd Edition; Scott, Foresman and Company: Glenview, IL, 1989; pp 43-53.
5. Silbey, R. J.; Alberty, R. A. *Physical Chemistry*, 3rd Edition; John Wiley & Sons: New York, 2001; pp 428-430, 615-618.

Useful Constants

$$N_A := 6.022 \cdot 10^{23} \quad \text{Avogadro's Number}$$

Introduction

The ideal gas law is an empirically determined expression that best describes gas behavior under conditions of high temperature and low pressure when intermolecular interactions are negligible. At high temperatures particles are moving too quickly for attractive forces to have a significant effect and at reduced pressures the large particle spacing precludes attractive or repulsive interactions of any consequence.

When conditions are such that deviations from ideal behavior occur, we need an alternative to the ideal gas law. An equation that is frequently used to describe the behavior of real gases is the virial equation of state, a polynomial expansion that may be expressed in terms of pressure or

molar volume, V_m . If we define the compression factor $Z = \frac{p \cdot V_m}{R \cdot T}$, the two forms of the virial equation are

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$

$$Z = 1 + B' \cdot p + C' \cdot p^2 + D' \cdot p^3 + \dots$$

In these expressions, the temperature-dependent parameters B, C, D, etc., are referred to as virial coefficients with each succeeding term in the expansion generally becoming increasingly less important. Note that for an ideal gas all coefficients are equal to zero and $Z = 1$.

Frequently we use experimental data to determine virial coefficients, but it is also important that we develop an understanding of the underlying factors that affect the values of these coefficients. Of significant interest is how these coefficients relate to molecular properties. Fortunately, statistical thermodynamics allows us to derive an expression that shows the relationship between the second virial coefficient and the intermolecular potential that represents the interaction between two particles. This expression is

$$B(T) = -2 \cdot \pi \cdot N_A \cdot \int_0^{\infty} \left(e^{\frac{-U(r)}{k \cdot T}} - 1 \right) \cdot r^2 \, dr \quad (1)$$

In this equation, $U(r)$ represents the intermolecular potential energy, k is the Boltzmann constant, and N_A is Avogadro's number. In the sections that follow, we will examine how the nature of this potential affects the calculated value of B . As a final exercise, we will use calculated values of B to explore the temperature dependence of Z , a parameter that may be calculated directly from experimental measurements.

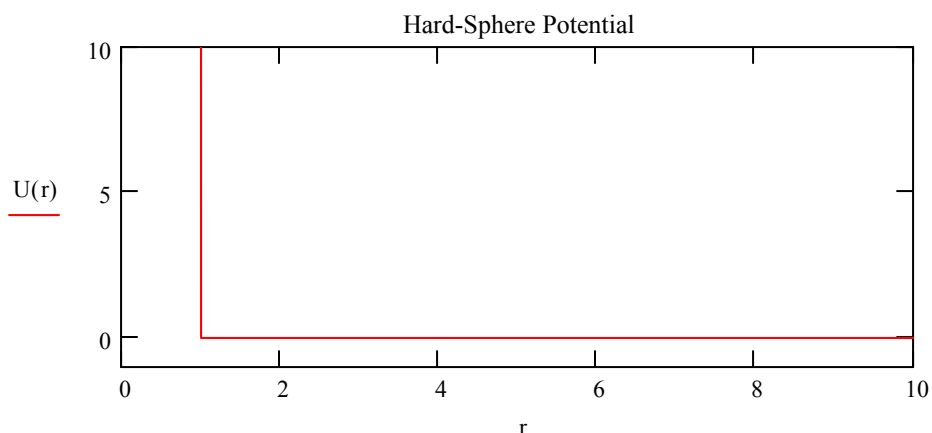
Hard-Sphere Potential

The simplest intermolecular potential is the hard-sphere potential. This potential assumes that particles behave like billiard balls, hard spheres that undergo completely elastic collisions. The functional form of the hard-sphere potential is shown below. In this expression, r is the distance separating the particle centers and d_{hard} represents the diameter of the sphere.

$$U(r) := \begin{cases} \infty & r < d_{\text{hard}} \\ 0 & \text{if } r > d_{\text{hard}} \\ \infty & \text{otherwise} \end{cases}$$

(2) **The hard-sphere diameter is set arbitrarily to 1 in the function definition for the purpose of graphing. It may be changed as indicated in question 3 below.**

Instructor's Note: Some displays may require that you adjust the dimensions of the plot to get the sharp repulsive edge to appear.



Questions:

1. What feature of this plot represents hard-sphere repulsion? Is attraction accounted for at all in the hard-sphere potential?

Instructor's Note: Clearly, the hard-sphere potential does not account for attraction; it does not show the potential well associated with attractive interactions.

2. Change the value of d_{hard} in the function definition above. How is the potential affected by this change?

Hard-Sphere Potential and the Second Virial Coefficient

Now let's derive an expression for the second virial coefficient based on the hard-sphere potential. We start with equation (1) introduced earlier.

$$B(T) = -2 \cdot \pi \cdot N_A \cdot \int_0^{\infty} \left(e^{\frac{-U(r)}{k \cdot T}} - 1 \right) \cdot r^2 \, dr$$

Because $U(r)$ is a discontinuous function, we must split the integral into two parts.

$$B(T) = -2 \cdot \pi \cdot N_A \cdot \left[\int_{d_{\text{hard}}}^{\infty} \left(e^{\frac{-0}{k \cdot T}} - 1 \right) \cdot r^2 \, dr + \int_0^{d_{\text{hard}}} \left(e^{\frac{-\infty}{k \cdot T}} - 1 \right) \cdot r^2 \, dr \right] \quad (3)$$

We will evaluate each of the integrals in this expression separately in the exercises below.

Problems:

1. Copy and paste the first of these integrals into the space below. Use the symbolic function to evaluate it.

$$\int_d^\infty \left(\frac{-0}{e^{k \cdot T} - 1} \right) \cdot r^2 dr \rightarrow 0$$

2. To evaluate the second integral we need to first determine the limit of the exponential term. Type your answer into the placeholder below.

$$\lim_{x \rightarrow \infty} e^{\frac{-x}{k \cdot T}} = \blacksquare$$

$$\lim_{x \rightarrow \infty} e^{\frac{-x}{k \cdot T}} = 0$$

3. Now, we can evaluate the integral. Substitute the limit value entered above for the exponential term in the second integral and solve symbolically.

$$\int_0^{d_{\text{hard}}} (0 - 1) \cdot r^2 dr \text{ simplify } \rightarrow \frac{-1}{3} \cdot d_{\text{hard}}^3$$

4. Combine your results from problems 1 and 3 to determine the overall expression for B(T).

$$B(T) = \frac{2 \cdot \pi \cdot N_A \cdot d_{\text{hard}}^3}{3}$$

Instructor's Note: This expression for B is referred to as the excluded molar volume and represents, for one mole of particles, the volume of space unavailable for motion due to the finite (non negligible) particle size. To understand this, consider two hard spheres of diameter d_{hard} . Their surfaces will touch when their centers are separated by d_{hard} . The hard surfaces resist further penetration (the potential rises to infinity) so the centers can come no closer than this, leaving a spherical region of space of radius d_{hard} that is unavailable for particle motion. For each pair of particles this volume is

equal to $\frac{4 \cdot \pi \cdot d_{\text{hard}}^3}{3}$. For one mole of particles or $N_A/2$ particle pairs, the total unavailable

volume is $\frac{2 \cdot N_A \cdot \pi \cdot d_{\text{hard}}^3}{3}$. It is interesting to note that this is also equal to the van der

Waals coefficient b for a gas consisting of hard spheres. See Noggle (reference 4 above) for more information.

5. Discuss the intermolecular interactions accounted for by the hard-sphere model and explain why the expression for B is independent of temperature.

Instructor's Note: As indicated in the introduction, temperature effects are largely related to attractive interactions. Consequently, the absence of attraction in the hard-sphere model leads to a result that is independent of temperature.

6. What assumptions regarding intermolecular interactions prevent the computed hard-sphere value of B from having a value less than zero?

Instructor's note: B is less than zero when attractive interactions dominate.

7. Use the hard-sphere diameter listed below to compute the value of B for Ar. Express your answer in units of L/mol.

$$d_{\text{hard}} := 316.2 \quad \text{Units of pm}$$

$$B_{\text{hard}} := - \left[2 \cdot \pi \cdot N_A \cdot \left(\frac{-1}{3} \cdot d_{\text{hard}}^3 \right) \right]$$

$$B_{\text{hard}} = 3.987 \times 10^{31} \quad \text{Units of pm}^3/\text{mol}$$

Conversion to L/mol requires multiplication by a factor of 10^{-33} .

$$B_{\text{hard}} := B_{\text{hard}} \cdot 10^{-33} \quad B_{\text{hard}} = 3.987 \times 10^{-2} \quad \text{Units of L/mol}$$

8. Use the expression given below to compute hard-sphere value of Z at a molar volume of 1.0 L/mol. Is the compression factor greater than or less than 1? What does this tell you about effect of intermolecular interactions on Z?

$$Z = 1 + \frac{B}{V_m}$$

$$Z := 1 + \frac{B_{\text{hard}}}{1}$$

$$Z = 1.04$$

Instructor's Note: Z is greater than one when repulsive forces dominate as is the case for the hard-sphere potential which neglects attractive interactions.

Square-Well Potential

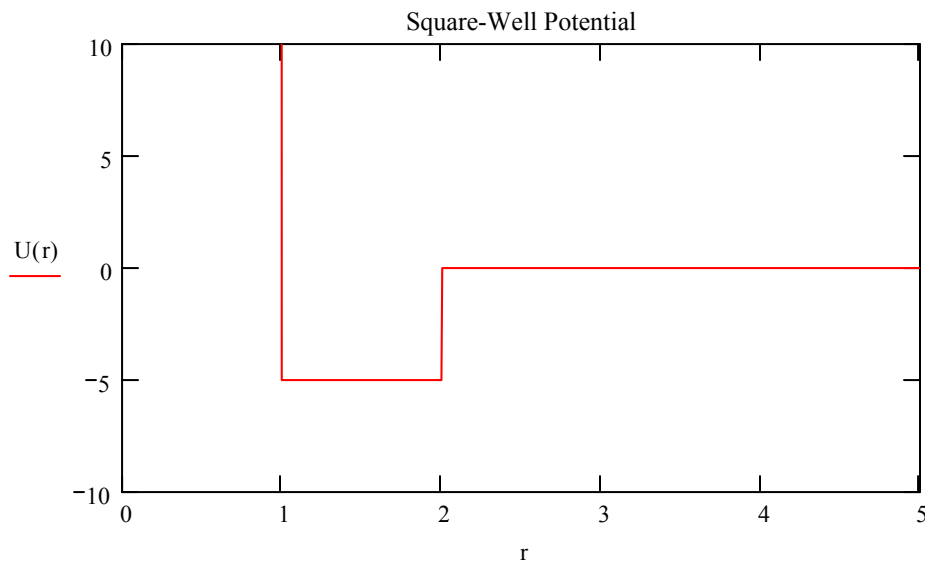
The next step in our attempt to approximate intermolecular interactions is the square-well potential. Like the hard-sphere potential, the square-well potential assumes particles to be hard spheres in the sense that potential rises to infinity when the hard surfaces contact; this happens when the particle centers are separated by a distance equal to the diameter d . However, this potential approximates intermolecular attraction with a rectangular well. The well depth is specified by the parameter ε and the width of the well is generally specified by the product $\lambda \cdot d$, where λ is an empirically determined parameter.

$$U(r) := \begin{cases} \varepsilon_{\text{square}} \leftarrow 5 \\ \lambda \leftarrow 2 \\ d_{\text{square}} \leftarrow 1 \\ 0 & \text{if } r > \lambda \cdot d_{\text{square}} \\ \infty & \text{if } r < d_{\text{square}} \\ -\varepsilon_{\text{square}} & \text{otherwise} \end{cases}$$

(4)

As before, parameters ε , λ , and d are defined arbitrarily within the function so that they remain undefined outside the definition.

Instructor's Note: As noted above, you may need to adjust the dimensions of the plot below to get the sharp repulsive edge to appear.



Problems:

1. Adjust values of ϵ , d , and λ . Describe what happens to the potential when you change each of these parameters.

2. Now let's derive the expression for the second virial coefficient based on the square-well potential. Following the model we used for the hard sphere, separate the integral from equation (1) into a sum of integrals with limits based on the square-well definition.

$$B_{\text{square}}(T) = 2 \cdot \pi \cdot N_A \cdot \left[\int_{\lambda \cdot d}^{\infty} \left(\frac{-0}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right) \cdot r^2 \, dr + \int_0^{\lambda \cdot d_{\text{square}}} \left[\frac{-(-\epsilon_{\text{square}})}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right] \cdot r^2 \, dr + \int_0^{d_{\text{square}}} \left(\frac{-\infty}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right) \cdot r^2 \, dr \right]$$

3. Derive expressions for each of the integrals in the sum.

$$\int_{\lambda \cdot d_{\text{square}}}^{\infty} \left(\frac{-0}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right) \cdot r^2 \, dr \text{ simplify } \rightarrow 0$$

$$\int_0^{d_{\text{square}}} \left(\frac{-\infty}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right) \cdot r^2 \, dr = \frac{1}{3} \cdot d_{\text{square}}^3$$

These two integrals are identical in form to those for the hard-sphere.

$$\int_0^{\lambda \cdot d_{\text{square}}} \left[\frac{-(-\epsilon_{\text{square}})}{e^{\frac{k \cdot T}{k \cdot T}} - 1} \right] \cdot r^2 \, dr \text{ simplify } \rightarrow \frac{1}{3} \cdot \lambda^3 \cdot d_{\text{square}}^3 \cdot \exp\left(\frac{\epsilon_{\text{square}}}{k \cdot T}\right) - \frac{1}{3} \cdot \lambda^3 \cdot d_{\text{square}}^3$$

4. Use the integral expressions from problem 3 to derive an overall expression for B(T).

$$B_{\text{square}}(T) = \frac{2 \cdot \pi \cdot N_A \cdot d_{\text{square}}^3}{3} \cdot \left[1 - (\lambda^3 - 1) \cdot \left(e^{\frac{\varepsilon_{\text{square}}}{kT}} - 1 \right) \right]$$

Instructor's note: You may choose to have students work this out on paper.

5. Use the data given below to plot B vs. T for both Ar and CO₂.

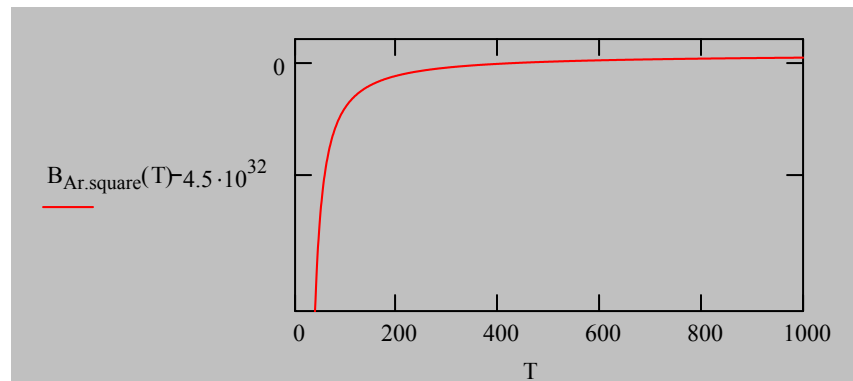
For Ar, we have

$$\varepsilon_{\text{rel}_{\text{Ar}}} := 69.4 \quad \text{The constant } \varepsilon_{\text{rel}} \text{ is equal to } \varepsilon/k \text{ and has units of K.}$$

$$\lambda_{\text{Ar}} := 1.85$$

$$d_{\text{Ar}} := 316.2 \quad \text{Units of pm}$$

$$B_{\text{Ar.square}}(T) := \frac{2 \cdot \pi \cdot N_A \cdot d_{\text{Ar}}^3}{3} \cdot \left[1 - \left[(\lambda_{\text{Ar}})^3 - 1 \right] \cdot \left(e^{\frac{\varepsilon_{\text{rel}_{\text{Ar}}}}{T}} - 1 \right) \right]$$



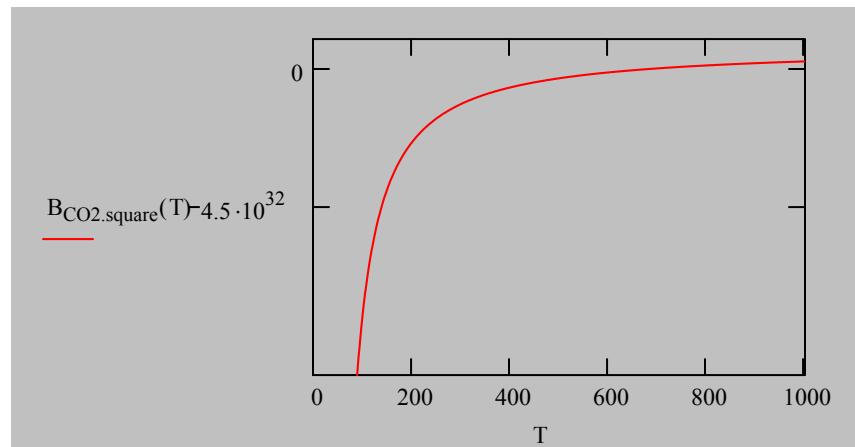
For carbon dioxide, we have

$\epsilon_{\text{relCO}_2} := 119$ **As before, the constant ϵ_{rel} is equal to ϵ/k and has units of K.**

$\lambda_{\text{CO}_2} := 1.83$

$d_{\text{CO}_2} := 391.7$ **in pm**

$$B_{\text{CO}_2.\text{square}}(T) := \frac{2 \cdot \pi \cdot d_{\text{CO}_2}^3 \cdot N_A}{3} \cdot \left[1 - \left(e^{-\frac{\epsilon_{\text{relCO}_2}}{T}} - 1 \right) \cdot (\lambda_{\text{CO}_2}^3 - 1) \right]$$



6. Use the data given above to compute $B(T)$ for argon and carbon dioxide at 273 K and 373 K. Express your answers in units of L/mol.

For Ar at 273 K and 373 K, we have

$$B_{\text{Ar.square}}(273) = -2.166 \times 10^{31} \text{ Units of pm}^3/\text{mol}$$

$$B_{\text{Ar.square}}(373) = -3.6 \times 10^{30} \text{ Units of pm}^3/\text{mol}$$

To convert to L/mol, we need to multiply by a factor of 10^{-33} .

$$B_{\text{Ar.square}}(T) := B_{\text{Ar.square}}(T) \cdot 10^{-33}$$

$$B_{\text{Ar.square}}(273) = -0.022 \text{ Units of L/mol}$$

$$B_{\text{Ar.square}}(373) = -3.600 \times 10^{-3} \text{ Units of L/mol}$$

For carbon dioxide at 273 K and 373 K, we have

$$B_{\text{CO}_2, \text{square}}(273) = -1.366 \times 10^{32} \text{ Units of pm}^3/\text{mol}$$

$$B_{\text{CO}_2, \text{square}}(373) = -7.029 \times 10^{31} \text{ Units of pm}^3/\text{mol}$$

Converting to L/mol, we get

$$B_{\text{CO}_2, \text{square}}(T) := B_{\text{CO}_2, \text{square}}(T) \cdot 10^{-33}$$

$$B_{\text{CO}_2, \text{square}}(273) = -0.137 \text{ Units of L/mol}$$

$$B_{\text{CO}_2, \text{square}}(373) = -0.0703 \text{ Units of L/mol}$$

7. Compare the values of B for Ar at these two temperatures. Provide an explanation for the difference. Do the same for CO₂.

Instructor's note: B is more negative at lower temperatures. This is indicative of the increased importance of attractive interactions as the temperature is reduced.

8. Compare the values of B for Ar and CO₂ at 373 K. Provide an explanation for the difference between the values for these two substances.

Instructor's note: The more negative values for carbon dioxide are indicative of stronger attractive interactions. This is reflected by the larger value of ϵ for carbon dioxide and is consistent with our prediction that carbon dioxide will have stronger induced-dipole interactions.

9. Compare the hard-sphere and square-well values of B for Ar. Provide an explanation for the difference.

Instructor's note: At these temperatures, the square-well value of B is negative. As indicated above, B is always greater than zero for the hard-sphere potential. The difference is simply due to the fact that attractive interactions are accounted for in the square-well potential but not in the hard-sphere potential.

10. Determine the high temperature limit for the square-well expression for B that you derived in problem 4 above. How does this compare to the hard-sphere expression? Provide an explanation for this.

Instructor's note: The expression derive above is

$$B_{\text{square}}(T) = \frac{2 \cdot \pi \cdot N_A \cdot d_{\text{square}}^3}{3} \cdot \left[1 - \left(\lambda^3 - 1 \right) \cdot \left(e^{-\frac{\epsilon_{\text{square}}}{kT}} - 1 \right) \right]$$

At high temperatures the exponential term $e^{-\frac{\epsilon_{\text{square}}}{kT}}$ approaches 1 and the above equation reduces to

$$B_{\text{square}}(T) = \frac{2 \cdot \pi \cdot N_A \cdot d_{\text{square}}^3}{3}$$

This, of course, is identical to the hard-sphere equation and is due to the reduced importance of attractive interactions as the temperature is increased.

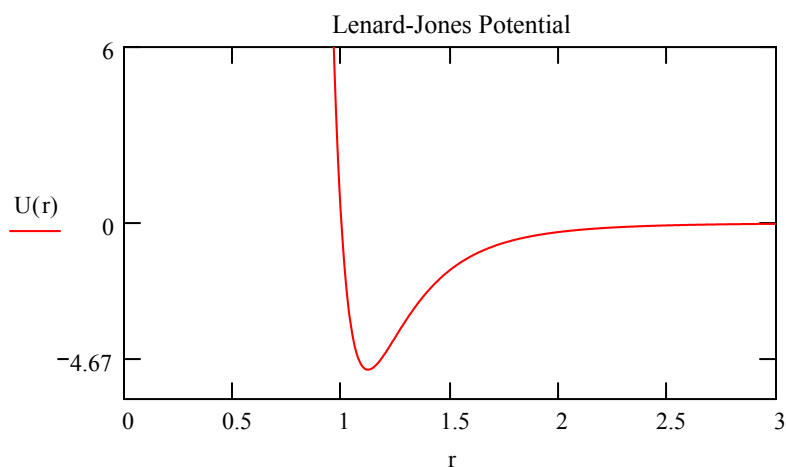
Students may also calculate the value of B at high temperatures for Ar and note that the high temperature limit is identical to the value obtained for Ar using the hard-sphere model.

Lennard-Jones Potential

Perhaps, the most widely-used potential that accounts for continuous changes in both the long-range attractive and short-range repulsive forces is the Lennard-Jones potential. Similar to the square-well potential, the Lennard-Jones description of intermolecular interactions uses two parameters, ϵ and d . As before, ϵ represents of the depth of the potential well and is indicative of the strength of attractive interactions. The parameter d represents the size of the molecules. In the equations below, we assign arbitrary values to ϵ and d for the purposes of graphing.

$$U(r) := \begin{cases} d_{LJ} \leftarrow 1 \\ \epsilon_{LJ} \leftarrow 5 \\ 4 \cdot \epsilon_{LJ} \left[\left(\frac{d_{LJ}}{r} \right)^{12} - \left(\frac{d_{LJ}}{r} \right)^6 \right] \end{cases} \quad (5) \quad \text{Again } d_{LJ} \text{ and } \epsilon_{LJ} \text{ values are set locally within the program block for the purpose of graphing the function.}$$

Note that the first term in the expression is positive with a large exponential factor of 12 whereas the second term is negative with a much smaller exponential factor of 6. The significance of each of these terms is explored in the questions below. A graph of the Lennard-Jones potential is shown below.



Questions:

1. Adjust values of ϵ and d in the LJ potential definition. How does the potential change when these parameters are changed?

2. Adjust the exponents in the LJ equation and note changes in the potential shape. Which of the two terms in the expression corresponds to intermolecular attraction and which corresponds to repulsion?

3. What is the value of $U(r)$ when $r = d_{LJ}$?

$$4 \cdot \epsilon_{LJ} \cdot \left[\left(\frac{d_{LJ}}{r} \right)^{12} - \left(\frac{d_{LJ}}{r} \right)^6 \right] \text{ substitute, } r = d_{LJ} \rightarrow 0$$

4. Derive an expression for r at the potential minimum.

$$\frac{d}{dr} 4 \cdot \epsilon_{LJ} \left[\left(\frac{d_{LJ}}{r} \right)^{12} - \left(\frac{d_{LJ}}{r} \right)^6 \right] = 0 \text{ solve, } r \rightarrow$$

$$\left[\begin{array}{c} \frac{1}{2^6} \cdot d_{LJ} \\ \left(\frac{1}{2} + \frac{1}{2} \cdot i \cdot 3^{\frac{1}{2}} \right) \cdot \frac{1}{2^6} \cdot d_{LJ} \\ \left(\frac{-1}{2} + \frac{1}{2} \cdot i \cdot 3^{\frac{1}{2}} \right) \cdot \frac{1}{2^6} \cdot d_{LJ} \\ -\frac{1}{2^6} \cdot d_{LJ} \\ \left(\frac{-1}{2} - \frac{1}{2} \cdot i \cdot 3^{\frac{1}{2}} \right) \cdot \frac{1}{2^6} \cdot d_{LJ} \\ \left(\frac{1}{2} - \frac{1}{2} \cdot i \cdot 3^{\frac{1}{2}} \right) \cdot \frac{1}{2^6} \cdot d_{LJ} \end{array} \right]$$

You may choose to have students do this on paper. From the results above, it is clear that the only acceptable solution is $r_{\min} = (1/2)^{1/6} d_{LJ}$.

5. How does the minimum potential energy relate to ϵ ?

$$U_{\min} = 4 \cdot \epsilon_{LJ} \left[\left(\frac{d_{LJ}}{r_{\min}} \right)^{12} - \left(\frac{d_{LJ}}{r_{\min}} \right)^6 \right] \text{ substitute, } r_{\min} = (2)^{\frac{1}{6}} \cdot d_{LJ} \rightarrow U_{\min} = -\epsilon_{LJ}$$

Lennard-Jones and the Second Virial Coefficient

The evaluation of the second virial coefficient from the Lennard-Jones is more complicated than that for other potentials. As before, we start with the integral

$$B(T) = -2 \cdot \pi \cdot N_A \cdot \left[\int_0^\infty \left(e^{\frac{-U(r)}{k \cdot T}} - 1 \right) \cdot r^2 dr \right]$$

Inserting the expression for the Lennard-Jones potential we get

$$B_{LJ}(T) = -2 \cdot \pi \cdot N_A \cdot \left[\int_0^\infty \left[\exp \left[\frac{-4 \cdot \varepsilon_{LJ} \cdot \left[\left(\frac{d_{LJ}}{r} \right)^{12} - \left(\frac{d_{LJ}}{r} \right)^6 \right]}{k \cdot T} \right] - 1 \right] \cdot r^2 dr \right] \quad (6)$$

Before we proceed, we will define reduced variables for temperature and distance.

$$\text{Reduced Temperature: } T_{\text{red}} = \frac{k \cdot T}{\varepsilon_{LJ}} \quad (7)$$

$$\text{Reduced Distance: } \rho = \frac{r}{d_{LJ}} \quad (8)$$

If we substitute these reduced variables into equation 6, we will need to integrate with respect to ρ instead of r . Consequently, we will also need to make the substitution

$$dr = d_{LJ} \cdot d\rho$$

After making these substitutions, we get

$$B_{LJ}(T) = -2 \cdot \pi \cdot d_{LJ}^3 \cdot N_A \cdot \int_0^\infty \left[\exp \left[\frac{-4 \cdot \left[(\rho)^{-12} - (\rho)^{-6} \right]}{T_{\text{red}}} \right] - 1 \right] \cdot \rho^2 d\rho \quad (9)$$

If we divide both sides of this equation by $\frac{2 \cdot \pi \cdot d_{LJ}^3 \cdot N_A}{3}$, we obtain

$$B_{\text{red}}(T_{\text{red}}) := -3 \cdot \int_0^\infty \left[\exp \left[\frac{-4 \cdot \left[(\rho)^{-12} - (\rho)^{-6} \right]}{T_{\text{red}}} \right] - 1 \right] \cdot \rho^2 d\rho \quad (10)$$

In this expression, B_{red} , the reduced second virial coefficient, is dimensionless and is related to B through the expression

$$B_{\text{red}}(T_{\text{red}}) = \frac{3 \cdot B(T)}{2 \cdot \pi \cdot d_{LJ}^3 \cdot N_A} \quad (11)$$

Note that equation 10 is a general expression that allows to investigate trends in $B_{\text{red}}(T_{\text{red}})$ regardless of particle identity.

Because we can't evaluate integral for B_{red} analytically, we will use the numerical algorithms embedded in MathCad. To determine the value of the reduced second virial coefficient at a specific reduced temperature, we simply enter the reduced temperature as shown below for a reduced temperature of 1.

$$B_{\text{red}}(1) = -2.538$$

Problems:

1. Compute B_{red} at several different reduced temperatures.

Instructor's note: Students may choose values arbitrarily to note trends.

$$B_{\text{red}}(3) = -0.115$$

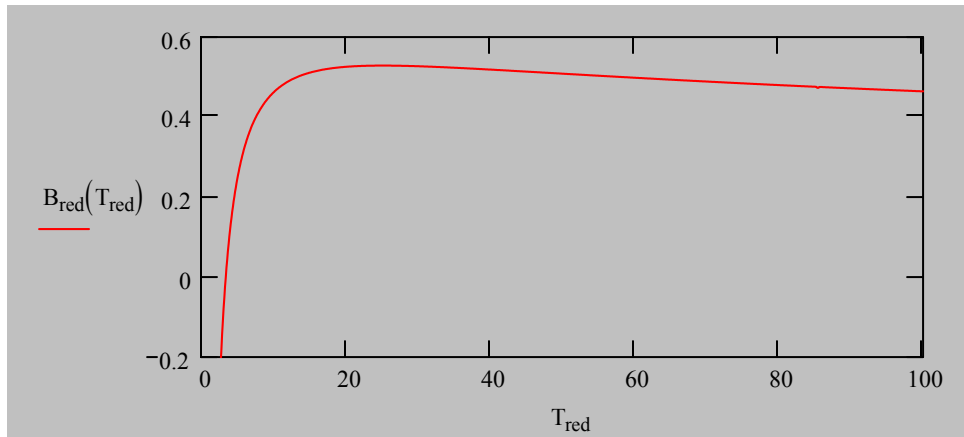
$$B_{\text{red}}(10) = 0.461$$

$$B_{\text{red}}(50) = 0.508$$

$$B_{\text{red}}(1000) = 0.294$$

$$B_{\text{red}}(100000) = 0.097$$

2. Plot B_{red} vs. T_{red} . What happens at low temperatures? Explain this temperature dependence in terms of intermolecular interactions.



Instructor's note: As was the case for the square potential, low temperatures yield negative values of B . This is consistent with our prediction that attractive interactions should dominate under these conditions.

3. What value does B_{red} approach at very high temperatures? Would you expect it to approach this value? Explain.

Instructor's note: The value approaches zero at high temperatures consistent with our prediction that a gas should behave ideally under these conditions.

4. We will now compute Lennard-Jones values of B for Ar and CO_2 at different temperatures. To do this we must first compute T_{red} for each of these substances at these temperatures. According to equation (7), the reduced temperature depends on T and ϵ_{LJ} . Use the Lennard-Jones parameters given below to determine T_{red} for Ar and CO_2 at 273 K.

$$\epsilon_{\text{relAr}} := 119.8$$

As before, the constant ϵ_{rel} is equal to ϵ/k and has units of K.

$$\epsilon_{\text{relCO}_2} := 189$$

Instructor's Solutions:

$$T := 273$$

For Ar, the reduced temperature is

$$T_{\text{Ar}}(T) := \frac{T}{\epsilon_{\text{relAr}}} \quad T_{\text{Ar}}(T) = 2.279$$

The reduced temperature is defined as a function here so that these expressions may be used later in the worksheet.

For carbon dioxide, we have

$$T_{\text{CO}_2}(\text{T}) := \frac{\text{T}}{\epsilon_{\text{relCO}_2}} \quad T_{\text{CO}_2}(\text{T}) = 1.444$$

5. Now use the values for the reduced temperatures computed above and equation (10) to calculate B_{red} for both Ar and CO_2 at 273 K.

For Ar, we have

$$B_{\text{red}}(T_{\text{Ar}}(\text{T})) = -0.432 \quad B_{\text{red}} \text{ is defined in equation 10.}$$

For carbon dioxide, we have

$$B_{\text{red}}(T_{\text{CO}_2}(\text{T})) = -1.294$$

6. Use the Lennard-Jones diameters listed below and equation (11) to calculate B (unreduced) for both Ar and CO_2 at 273 K. Express your final answers in units of L/mol.

$$d_{\text{Ar}} := 340.5$$

As before, diameter is expressed in units of pm.

$$d_{\text{CO}_2} := 448.6$$

After rearranging equation 11 and expressing B as a function of unknown parameters T_{red} and d, we get

$$B_{\text{LJ}}(T_{\text{red}}, d) := \frac{2 \cdot \pi \cdot d^3 \cdot N_{\text{A}}}{3} B_{\text{red}}(T_{\text{red}})$$

This allows us to compute the unreduced value of B.

For Ar, we get

$$B_{\text{LJ}}(T_{\text{Ar}}(\text{T}), d_{\text{Ar}}) = -2.152 \times 10^{31} \quad \text{Units of pm}^3/\text{mol}$$

As before, conversion to L/mol requires multiplication by a factor of 10^{-33} .

$$B_{\text{Ar.LJ}}(\text{T}) := B_{\text{LJ}}(T_{\text{Ar}}(\text{T}), d_{\text{Ar}}) \cdot 10^{-33}$$

$$B_{\text{Ar.LJ}}(\text{T}) = -0.02152 \quad \text{Units of L/mol}$$

For carbon dioxide, we have

$$B_{LJ}(T_{CO_2}(T), d_{CO_2}) = -1.474 \times 10^{32} \text{ Units of pm}^3/\text{mol}$$

In units of L/mol, we have

$$B_{CO_2.LJ}(T) := B_{LJ}(T_{CO_2}(T), d_{CO_2}) \cdot 10^{-33}$$

$$B_{CO_2.LJ}(T) = -0.1474 \text{ Units of L/mol}$$

7. Repeat questions 3 through 6 both Ar and CO₂ at 373 K.

$$T := 373$$

For Ar, the reduced temperature is

$$T_{Ar}(T) = 3.114$$

The corresponding value for B_{red} is

$$B_{red}(T_{Ar}(T)) = -0.08$$

And the value of B is

$$B_{LJ}(T_{Ar}(T), d_{Ar}) = -4.004 \times 10^{30} \text{ Units of pm}^3/\text{mol}$$

In units of L/mol, we have

$$B_{Ar.LJ}(T) := B_{LJ}(T_{Ar}(T), d_{Ar}) \cdot 10^{-33}$$

$$B_{Ar.LJ}(T) = -4.00411 \times 10^{-3} \text{ Units of L/mol}$$

Similarly for carbon dioxide, we have

$$T_{CO_2}(T) = 1.974$$

$$B_{red}(T_{CO_2}(T)) = -0.65$$

$$B_{LJ}(T_{CO_2}(T), d_{CO_2}) = -7.396 \times 10^{31} \text{ Units of pm}^3/\text{mol}$$

In units of L/mol, we have

$$B_{CO_2.LJ}(T) := B_{LJ}(T_{CO_2}(T), d_{CO_2}) \cdot 10^{-33}$$

$$B_{CO_2.LJ}(T) = -0.0740 \text{ Units of L/mol}$$

8. Discuss the differences between the values of B obtained for Ar and CO_2 at these two temperatures. How do the properties of these particles affect the values of B ?

Instructor's note: As indicated in the instructor's note to problem 8 in the square-well section above, the more negative values for carbon dioxide are indicative of stronger attractive interactions.

9. Summarize the differences between the three potentials explored in this exercise and compare the temperature dependence of B as predicted by each. Comment on the relative ability of each potential to accurately model molecular behavior. Experimental values of for argon and carbon dioxide are given below.

$$B_{\text{Ar}}(273) = -0.0217 \cdot \frac{\text{L}}{\text{mol}} \qquad B_{\text{Ar}}(373) = -0.0042 \cdot \frac{\text{L}}{\text{mol}}$$

$$B_{\text{CO}_2}(273) = -0.142 \cdot \frac{\text{L}}{\text{mol}} \qquad B_{\text{CO}_2}(373) = -0.0722 \cdot \frac{\text{L}}{\text{mol}}$$

Instructor's note: The hard-sphere potential leads to a value of B that is always greater than zero and independent of temperature. Clearly, this potential is the least accurate and will work only under those conditions that lead to insignificant attractive interactions (high temperatures). The differences between B -values obtained for the square-well and Lennard-Jones potentials at moderate temperatures are small. However, at high temperatures the two models diverge as the Lennard-Jones value for B approaches zero, whereas the square-well limit is a finite positive value. The Lennard-Jones high temperature limit is more consistent with our expectation that gases approach ideal behavior as the temperature increases. Based on this, we can see that while the square-well potential may be a useful approximation under certain conditions, the Lennard-Jones potential, as we should suspect, represents a more accurate model overall.

The Second Virial Coefficient and the Compression Factor

As a final exercise, we will use our expressions for B to examine the temperature dependence of the compression factor, Z, a factor that may be measured directly from experiment. To do this we need to use the truncated form of the expression for Z specified in the introduction.

$$Z = 1 + \frac{B}{V_m} \quad (12)$$

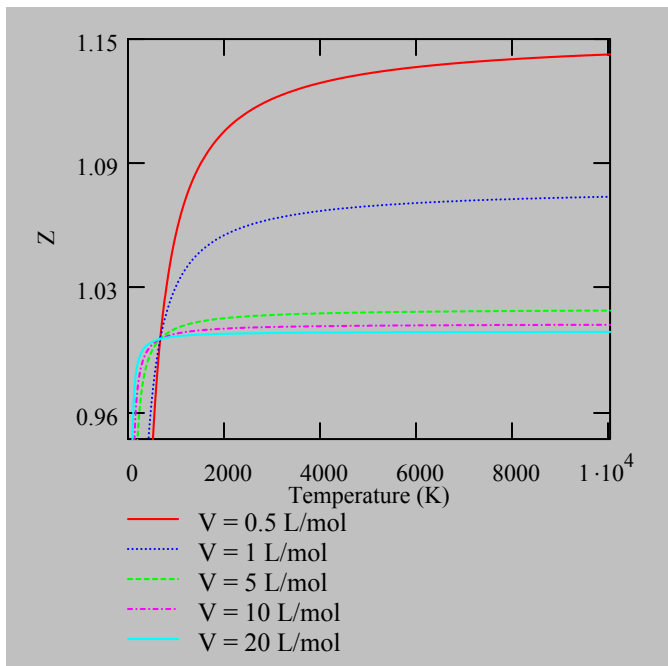
Because the hard-sphere potential leads to a temperature-dependent result, we will consider only the square-well and Lennard-Jones potentials in the problems below.

Problems:

1. Use the square-well expression for B to plot Z for CO₂ vs temperature at several volumes ranging from 0.5 L to 20 L.

$$Z_{\text{square}}(\text{Temp}, V_m) := 1 + \frac{B_{\text{CO2.square}}(\text{Temp})}{V_m}$$

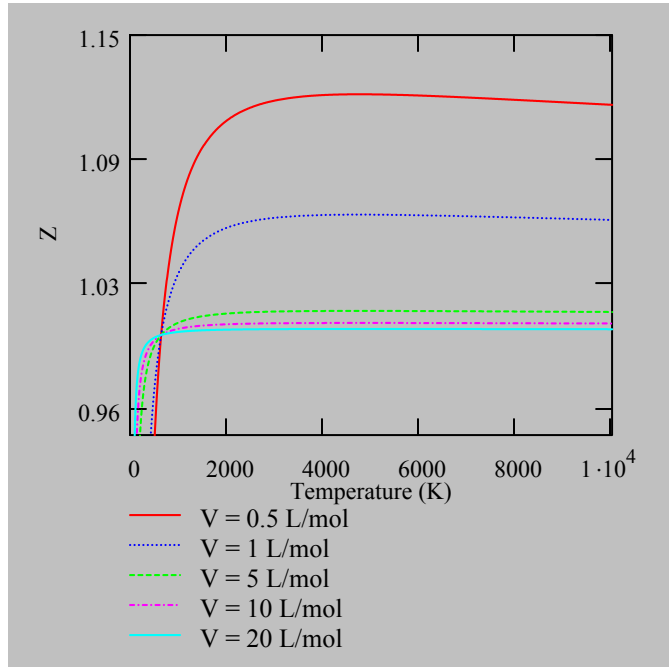
This uses the square-well expression for B that generates values with units of L/mol.



2. Repeat question 1 for the Lennard-Jones potential

$$Z_{LJ}(\text{Temp}, V_m) := 1 + \frac{B_{\text{CO2,LJ}}(\text{Temp})}{V_m}$$

This uses the Lennard-Jones expression for B that generates values with units of L/mol.



3. Discuss the temperature dependent behavior of Z. Under what conditions is $Z > 1$? Under what conditions is it less than 1? How does this relate to B? Explain this in terms of intermolecular interactions.

Instructor's note: At low temperatures, $Z < 1$ because attractive interactions dominate and $B < 0$. As the temperature is increased, attractive interactions become less significant causing Z to increase as B increases. At intermediate to high temperatures, the value of Z exceeds 1 because repulsive interactions dominate and $B > 0$. At very high temperatures, we note that the Lennard-Jones value of Z approaches 1 as we would predict for an ideal gas with negligible interactions; at these temperatures B approaches a value of 0.

4. Compare the Z vs. T plots at different volumes. Explain differences in terms of intermolecular interactions.

Instructor's note: In each case, $Z < 1$ at low temperature and rises steadily as the temperature is increased. However, we note that as the volume is decreased the rate at which Z increases also decreases; smaller volumes require greater temperatures for Z to reach a value of 1. In addition, we note that the maximum value of Z is greater for smaller volumes. We can explain both of these observations in terms of intermolecular interactions. At low temperatures, the higher density of particles at low volumes enhances attractive interactions and higher temperatures are necessary to overcome these interactions. At high temperatures, when attractive interactions are negligible, the higher particle density leads to greater repulsion and a larger value of Z. Both the square-well and Lennard-Jones potentials predict this behavior.

