

# The Use of Second Virial Coefficients in Energy and Environmental Research

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- Condensation Repression
- Lennard-Jones Potential
- Mayer Function
- Morse Potential
- Second Virial Coefficient

ABSTRACT

The use of isotopically enriched materials is frequently used in energy and environmental research. One of the techniques of laser isotope enrichment, that using condensation repression, is influenced by the parameters of the inter-molecular potential. This is usually modeled by the Lennard-Jones potential. Described here is a technique by which the parameters of the potential may be approximated from the second virial coefficients of the gas.

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## INTRODUCTION

There is a need for isotopically enriched elements for energy production research, medical research, and other fields of science and technology. The condensation repression technique prevents, or represses, the formation of dimers by exciting vibrational states in gaseous molecules containing the isotope of interest. The molecules containing that specific isotope are prevented from condensing on the walls of a cooled container and thus the gaseous phase becomes increasingly enriched in the desired isotope.

Presented here is a “Brute-Force” technique for the estimation of the parameters of the Lennard-Jones potential<sup>1</sup> for a gas by comparison with its measured second virial coefficient. The Lennard-Jones potential is a model for the intermolecular potential as a function of separation distance. It has spherical symmetry and therefore implies no permanent dipole moment. The potential is shown below.

$$u(r) = 4u_0 \left[ \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^6 \right]$$

A graph of a Lennard-Jones potential and the parameters of interest are shown in figure 1. The goal is to choose an intermolecular separation as close to  $r_0$  as possible such that the only molecules that are repressed are those excited by a laser. Knowing  $u_0$  allows one to choose an excitation state that represses condensation but is insufficient to cause molecular disassociation. Unfortunately, the parameters of the Lennard-Jones Potential can not be directly measured.

The virial coefficients however, are a direct measure of the deviation of a real gas from a perfect gas.

They may be written:

$$P = \frac{NRT}{V} \left[ 1 + B(T) \left[ \frac{N}{V} \right] + C(T) \left[ \frac{N}{V} \right]^2 + \dots \right]$$

where the first virial coefficient (1) represents a perfect gas, the second,  $B(T)$  represents two body interactions,  $C(T)$  three body interactions, and so on.

For low density gases where:

$$\left[ \frac{N}{V} \right] \gg \left[ \frac{N}{V} \right]^2$$

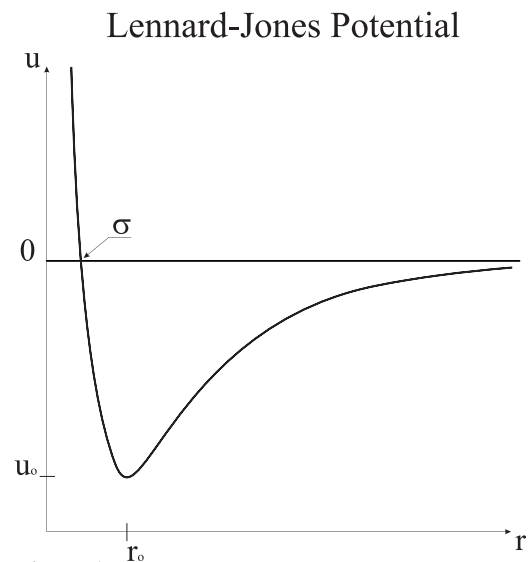


Figure 1:  
 $\sigma$  is the value of  $r$  where the potential is zero.  $r_0$  is the mean distance between molecules and where the slope of the potential is zero.  $u_0$  is the depth of the potential well.

only  $B(T)$  is of interest. The values of  $B(T)$  have been measured as a function of temperature for many gases.<sup>3</sup> A typical  $B(T)$  vs.  $T$  is shown in figure 2.

The relationship between the second virial coefficient and the Lennard-Jones potential is:<sup>4</sup>

$$B(T) = -2\pi \int_0^{\infty} r^2 f(r) dr$$

where  $f(r)$  is the Mayer function:<sup>4</sup>

$$f(r) = e^{\frac{-u(r)}{kT}} - 1$$

The objective of this note is to describe a method of extracting the parameters  $u_0$  and  $\sigma$ , or alternately  $r_0$ , from measured  $B(T)$ 's where:

$$r_0 = \sigma\sqrt[6]{2}$$

Consequently, the Lennard-Jones potential can be alternately written:

$$u(r) = u_0 \left[ \left[ \frac{r_0}{r} \right]^{12} - 2 \left[ \frac{r_0}{r} \right]^6 \right]$$

An important distinction to note is that the Lennard-Jones potential is not temperature dependant even though it can be derived from  $B(T)$ . The caveat to this statement is that the temperature of the gas in question is not so high as to excite any vibrational or rotational states in the molecules.

#### PROCEDURE

The first step is to choose a region in the parameter space<sup>2</sup> ( $u_0, \sigma$ ) to consider. Starting with  $\sigma$ , if one considers a molecule as a hard sphere,  $\sigma$  should be approximately equal to twice the covalent radius of any given molecule. This approach yields good starting values. Next, one must determine a starting point for  $u_0$ . It should be noted that the potential well depth should have a strong correlation with the boiling point of the substance. For identical spherical molecules,  $u_0$  is generally within 30% of the boiling point.

Considering values of  $\sigma$  that span  $\pm 10\%$  -  $20\%$  of the estimated separation distance and values

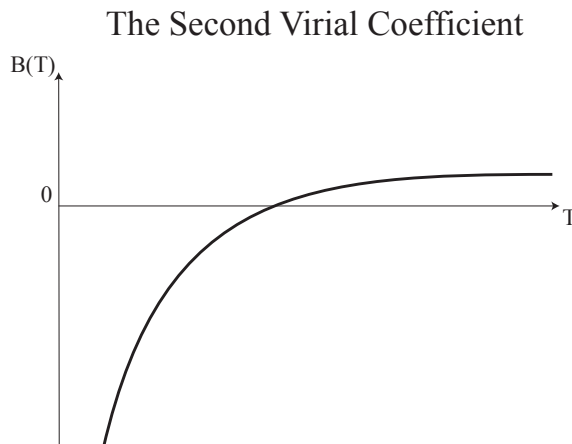


Figure 2:  
B(T) equal to zero is the Boyle temperature.

of  $u_0$  spanning + 30% of the boiling point, a grid or matrix can be generated for  $B(T)$  as shown below.

$$\begin{bmatrix} B(T)_{u_1\sigma_1} & \cdots & B(T)_{u_1\sigma_n} \\ \vdots & \ddots & \vdots \\ B(T)_{u_m\sigma_1} & \cdots & B(T)_{u_m\sigma_n} \end{bmatrix}$$

It should be noted that while  $u_0$  is a potential energy and the boiling point is a temperature they are proportionally related by the Boltzmann constant. Once the matrix is generated, a value of  $T_0$  for which  $B(T)$  is well known is chosen and each element is evaluated. If one stopped at this point and

plotted each row for constant  $T$  and  $u_0$ , one would obtain a set of plots similar to those shown in figure 3. Those plots that contain  $B(T_0)$  within the domain of the matrix are regions of interest for further evaluation. Next, the resultant matrix elements are each subtracted from the measured or known value of  $B(T_0)$  and then squared to facilitate a non-linear least squares fit. This transforms the original matrix from the parameter space  $(u_0, \sigma)$  to a matrix in  $\Delta^2$  space.

$$\begin{bmatrix} (\Delta_{u_1\sigma_1})^2 & \cdots & (\Delta_{u_1\sigma_n})^2 \\ \vdots & \ddots & \vdots \\ (\Delta_{u_m\sigma_1})^2 & \cdots & (\Delta_{u_m\sigma_n})^2 \end{bmatrix}$$

In the parameter space  $(u_0, \sigma)$ , the three points closest to the value of  $B(T_0)$  in each region are examined in  $\Delta^2$  space. Since the plots are not linear in the parameter space, they must be fitted in  $\Delta^2$  space where the three points in each region of interest will be approximately parabolic. The mapping from parameter space  $(u_0, \sigma)$  to  $\Delta^2$  space can be seen in figure 4. The parabolic fit can then be used to calculate the minimum values for  $u_0$  and  $\sigma$  in each region. Each set of values from each region of interest are then compared to all available known values of  $B(T)$  at varying temperatures. The set of  $u_0$  and  $\sigma$  that produce the  $B(T)$  plot

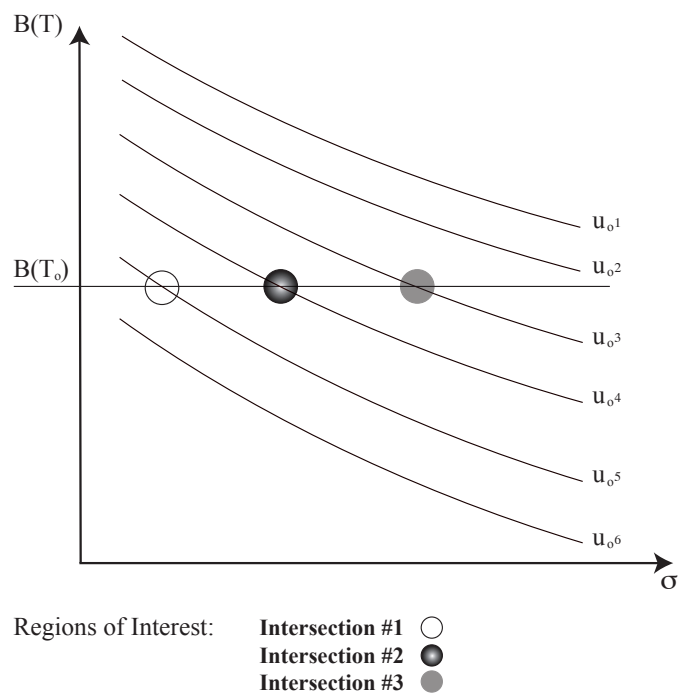


Figure 3:  
Each region of interest contains three plotted points closest to  $B(T_0)$ . See parameter space in figure 4.

with the smallest sum of the squared deviations are the values of  $u_0$  and  $\sigma$  that are deemed the acceptable Lennard-Jones parameters.

CONCLUSION

The Lennard-Jones parameter  $u_0$  is an approximation of the di-molecular disassociation energy which yields information concerning the maximum temperature for which condensation repression can take place. The parameter  $r_0$  is approximately the separation distance between the centers of mass, or one half the diameter of the di-molecule. This process works well for symmetric molecules. In the case of Xenon, the calculated parameters ( $u_0 = 214.25$  K,  $\sigma = 4.1999$  Å) produces values of  $B(T)$  within 5% of measured values as shown below in figure 5. Future research may involve adapting this technique to more realistic models such as the Morse potential.

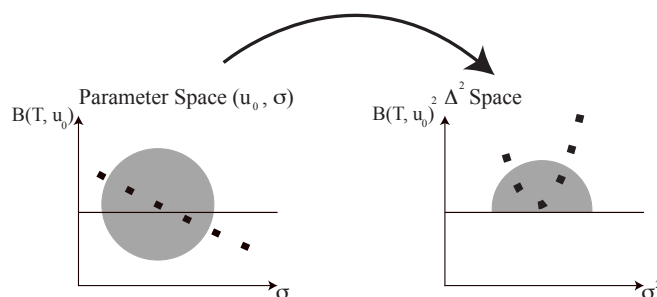


Figure 4: Transformation of a region of interest from parameter space to  $\Delta^2$  space.

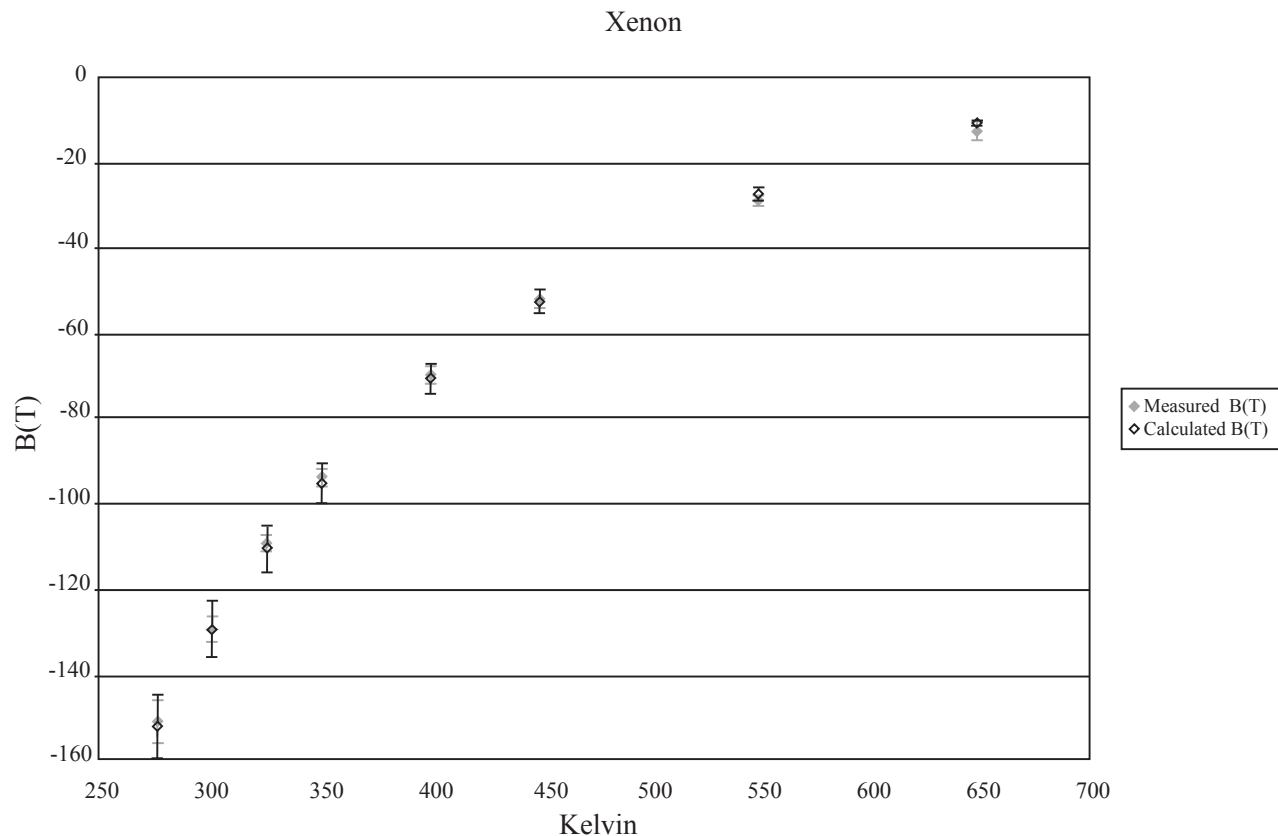


Figure 5: A comparison of the known measured values of  $B(T)$  for Xenon versus those calculated from the Lennard-Jones parameters using the “Brute-Force” technique described here.

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## FIGURE CAPTIONS

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