



Western Michigan University  
ScholarWorks at WMU

---

Master's Theses

Graduate College

---

12-1994

## Determination of the Bulk Modulus of a Lennard-Jones Solid

Spencer A. Van Roekel

Follow this and additional works at: [https://scholarworks.wmich.edu/masters\\_theses](https://scholarworks.wmich.edu/masters_theses)



Part of the Physics Commons

---

### Recommended Citation

Van Roekel, Spencer A., "Determination of the Bulk Modulus of a Lennard-Jones Solid" (1994). *Master's Theses*. 4273.

[https://scholarworks.wmich.edu/masters\\_theses/4273](https://scholarworks.wmich.edu/masters_theses/4273)

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact [wmu-scholarworks@wmich.edu](mailto:wmu-scholarworks@wmich.edu).



DETERMINATION OF THE BULK MODULUS  
OF A LENNARD-JONES SOLID

by

Spencer A. Van Roekel Jr.

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Physics

Western Michigan University  
Kalamazoo, Michigan  
December 1994

DETERMINATION OF THE BULK MODULUS  
OF A LENNARD-JONES SOLID

Spencer A. Van Roekel Jr., M.A.

Western Michigan University, 1994

The quantum Monte Carlo method is used to determine the bulk modulus of a Lennard-Jones solid. The quantum Monte Carlo method is discussed in detail and is compared with other numerical methods used previously.

The zero pressure bulk modulus of a Lennard-Jones solid is computed at a number of different temperatures and compared with experimental data.

## TABLE OF CONTENTS

LIST OF FIGURES.....	iii
CHAPTER	
I. INTRODUCTION.....	1
II. QUANTUM MONTE CARLO METHOD.....	8
III. RESULTS.....	16
IV. DISCUSSION.....	18
REFERENCES.....	29

## LIST OF FIGURES

1. Graph of Pressure Versus Lattice Constant for a Temperature of 14.98K.....	19
2. Graph of Pressure Versus Lattice Constant for a Temperature of 17.11K.....	20
3. Graph of Pressure Versus Lattice Constant for a Temperature of 19.97K.....	21
4. Graph of Pressure Versus Lattice Constant for a Temperature of 23.96K.....	22
5. Graph of Pressure Versus Lattice Constant for a Temperature of 29.95K.....	23
6. Graph of Pressure Versus Lattice Constant for a Temperature of 39.93K.....	24
7. Graph of Pressure Versus Lattice Constant for a Temperature of 59.90K.....	25
8. Graph of Zero Pressure Bulk Modulus Versus Temperature of Calculated and Experimental Results.....	26

## CHAPTER I

### INTRODUCTION

The purpose of this thesis is to look at the quantum Monte Carlo simulation as a means to study the thermodynamic properties of inert gas solids arising from atomic motion (vibrations). More specifically, this thesis aims at comparing the zero pressure bulk modulus of a Lennard-Jones pair potential (using nearest neighbor interactions calculated from the quantum Monte Carlo method) to experimental data. The quantum Monte Carlo method is in some respects found to be much better than previous methods that have been used to treat these properties. The previous methods of studying such systems have a rather long history (60 years) while the quantum Monte Carlo method is only a recent development (last 20 years) and its application to study the vibrational properties of solids, particularly those of the inert gas solids has only been made in the last 3 years. Some of the methods that have been used in the long history of lattice vibrations include: (a) exact enumeration, (b) perturbation techniques, and (c) classical Monte Carlo method. Each of these methods has its relative strengths and weaknesses in solving for the properties of our thermodynamic system but as we shall see below the

quantum Monte Carlo method offers potential for an accurate (essentially exact) treatment which is not within the scope of previous approximate treatments. The purpose of this introduction will be to give a brief synopsis of the methods, including the quantum Monte Carlo, which have been used to study lattice vibrations of inert gas systems and to outline the problem addressed in this thesis. We will begin by discussing inert gas systems and why they are of interest to us.

The inert gas solids are of particular interest for a number of reasons:

1. The inert gas solids form the simplest crystals with the weakest and best known atomic bonding characteristics. All inert gas solids have a face-centered cubic structure which is a close packing structure arising from nondirectional Van der Waals forces. This arrangement has an atom at each corner of the cube and one centered on each face of the cube. This structure yields the most optimum volume packing.

2. Inert gas solids have very weak short range interactions, as is indicated from their low melting point. These short range interactions are called Van der Waals forces and arise from instantaneously induced dipole moments between pairs of neighboring inert gas atoms. Van der Waals forces provide very little distortion for the

electron cloud from the free space atomic configuration and are easily computed theoretically. The other bonding mechanisms in crystals (metallic, ionic, and covalent) all are much more difficult to characterize and are hence less well understood than the Van der Waals interaction in inert gas solids. In metallic bonding the valence electrons form a Fermi liquid of electrons in the metal and the precise nature of this Fermi liquid is difficult to characterize. The interatomic bonding is due to a decrease in the kinetic energy of the valence electrons and the electrons move all over the solid. The bonding in these systems represents a complex many body problem where the motion of one atom affects many other atoms through an interaction mediated by the electron gas. In ionic bonding, on the other hand, charges alternate in the crystal structure and interact via long range coulomb forces. The long range forces make this a complicated many body problem also. In covalent bonding, there are many shared electrons and much distortion in the electron cloud. The potentials of the inert gas solids which are of interest to us are the weak short ranged pair potentials given to a high degree of accuracy by the Lennard-Jones form. (A pair potential is the interaction between pairs of nearest neighboring atoms.)

The quantum Monte Carlo simulation of vibrational properties of solids is a modification of past classical



methods to now correctly treat the true quantum nature of such problems. Within the past 20 years quantum Monte Carlo simulations on quantum systems have been found feasible having been initially applied to spin and many fermion systems and only recently to vibrational systems. The difficulty in simulating quantum vibrational systems comes from the numerical evaluation of properties derived from the quantum mechanical partition function. This difficulty is due to the noncommutivity of the operators in the quantum partition function.

In the quantum Monte Carlo method we shall discuss a device known as the Trotter identity which maps the quantum mechanical partition function onto that of a corresponding classical system. This allows us to apply standard classical Monte Carlo methods to the mapped classical system in evaluating the properties of the quantum mechanical system.

Using these methods Suzuki(1976) showed that a  $d$ -dimensional quantum system can be converted to a  $d+1$ -dimensional classical system, and one can then use Monte Carlo simulation techniques for classical systems to evaluate this  $d+1$ -dimensional system. The eventual application of the quantum Monte Carlo simulation that we shall pursue is to find the pressure and bulk modulus of a many body quantum vibrational system and to compare that data with experimental results.

Before the Monte Carlo simulation technique the most common way to study the thermodynamic properties of a many body problem was through exact enumeration of configurations in computing the partition function, or approximation techniques, such as perturbation theory and other analytic treatments. Exact enumeration requires knowing the probability of occurrence of all the different states of a system at some temperature. One can easily see, however, that this can only be done on a system of relatively few particles. The more particles that are involved, the more states that a particular system can have. The number of states grows in a combinatorial fashion as a function of the number of particles thereby making enumeration impossible even on the fastest computer for large systems.

The classical Monte Carlo method, on the other hand, uses a technique called Metropolis sampling, or importance sampling. This involves taking a representative sample of particular states in a system based on the relative weight, or importance, that state has on the calculation of the partition function. This is done by using a Markovian process in which a state of the system is chosen at random. This state is then given a probability based on the importance it has in determining the partition function. A transition probability is then defined as the probability that state has to overcome before it is accepted. If the

probability of the state generated is greater than the transition probability, then it is accepted, otherwise it is rejected. This process of finding one acceptable state accounts for one Monte Carlo step. As more Monte Carlo steps are done, one gets a sampling of acceptable states. With this sampling of states one can then determine the thermodynamic properties of the system.

Though this is a much better way of determining the partition function of a many body problem than with the method of exact enumeration, there are still problems with this method. The most obvious one, which was assumed from the beginning, was the lack of the true quantum nature of the system. Also, since a truly infinite system is not being used the nature of the phase transitions of the system are not fully realized.

In the 1970's Suzuki(1976), using Trotter's identity, showed in general that a  $d$ -dimensional quantum system can be mapped onto a  $d+1$ -dimensional classical system. By the use of this mapping one can then use the classical Monte Carlo method just described. This method can be used on both Fermi and Bose systems of particles. The implementation of this method on either a Bose or Fermi system creates difficulties in either system that have to be overcome. When using the Monte Carlo method on Fermi systems, one can run into trouble getting a negative

partition function by the very nature of how the partition function is calculated using this technique. In Bose systems, on the other hand, a good transition probability matrix is very difficult to find. Part of the reason stems from the fact that it is impossible to generate the permutation moves needed in Bose systems without changing the position. Each of these problems had to be overcome before implementing the Monte Carlo technique. A number of different many body problems have been studied using the quantum Monte Carlo method. Barma and Shastri (1978) have used this method to study spin systems. Hirsch, et al. (1981,1982) have studied fermion systems, in particular the Hubbard model, by the implementation of this method. Ceperley, et al. (1986,1987) has used this method to study both the Fermi and Bose characteristics of liquid helium. Each of these studies on particular systems has been helpful in either proving or disproving a particular theory by comparing with experimental results. Of more recent interest in the use of this method is the study of lattice vibrations. Of particular interest in this system will be to compute the bulk modulus using the three dimensional Lennard-Jones model. This will be explained in Chapters II and III.

## CHAPTER II

### QUANTUM MONTE CARLO METHOD

To introduce the quantum Monte Carlo method, consider a single quantum mechanical particle in one dimension. This will serve to generalize the problem to three dimensions. The motion of this particle is described by the Hamiltonian operator,  $H$  which consists of two terms: (1) a kinetic energy term

$$H_o = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (1)$$

and (2) a potential energy term

$$H_1 = V(x) \quad (2)$$

The resulting Hamiltonian then becomes

$$H = H_o + H_1 \quad (3)$$

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (4)$$

$H$  operates on a wave function  $\Psi_n(x)$  to yield the eigenvalue equation

$$H\Psi_n(x) = E_n\Psi_n(x) \quad (5)$$

We will show how to compute three physical quantities energy,  $U$ , the specific heat at constant volume,  $C_v$ , and the bulk modulus,  $M_B$ . To calculate these physical quantities, the partition function needs to be used. The partition function is defined as

$$Z = \text{tr}(e^{-\beta H}) = \text{tr}(e^{-\beta(H_0 + H_1)}) \quad (6)$$

where

$$\beta = \frac{1}{k_B T} \quad (7)$$

$k_B$  is the Boltzmann constant and  $T$  is the temperature in Kelvin. From the partition function, the energy  $U$  is found by

$$U = -\frac{\partial}{\partial \beta} \ln Z \quad (8)$$

the specific heat by

$$C_v = \frac{\partial U}{\partial T} \quad (9)$$

and the bulk modulus by

$$M_B = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (10)$$

As previously discussed, the Suzuki-Trotter method takes a  $d$ -dimensional quantum system and maps it onto a

d+1-dimensional classical system. This is done using the Trotter identity. We shall now discuss the Trotter identity and then show how it can be used to get the mapping of the quantum mechanical to classical mechanical partition function.

The Trotter identity is stated as follows. For any two operators A and B with

$$[A, B] \neq 0 \quad (11)$$

$$e^A e^B = \lim_{M \rightarrow \infty} (e^{\frac{(A+B)}{M}})^M \quad (12)$$

When using this identity the partition function becomes

$$Z = \lim_{M \rightarrow \infty} \sum_{n=0}^{\infty} \langle n | (e^{-\frac{\beta}{M}(H_0+H_1)})^M | n \rangle \quad (13)$$

$$Z = \sum_{n=0}^{\infty} \langle n | [e^{-\frac{\beta}{M}(H_0+H_1)}] [e^{-\frac{\beta}{M}(H_0+H_1)}] \dots [e^{-\frac{\beta}{M}(H_0+H_1)}] | n \rangle \quad (14)$$

and inserting a complete set of states

$$H | n \rangle = E_n | n \rangle \quad (15)$$

we find

$$Z = \sum_{n=0}^{\infty} \langle n | e^{-\frac{\beta}{M}H_0} e^{-\frac{\beta}{M}H_1} | m \rangle \langle m | e^{-\frac{\beta}{M}H_0} e^{-\frac{\beta}{M}H_1} | n \rangle \dots$$

$$\dots \langle m | e^{-\frac{\beta}{M} H_0} e^{-\frac{\beta}{M} H_1} | m \rangle + O\left(\frac{1}{M^2}\right) \quad (16)$$

where we use

$$\langle m | e^{-\frac{\beta}{M} (H_0 + H_1)} | n \rangle = \langle m | e^{-\frac{\beta}{M} H_0} e^{-\frac{\beta}{M} H_1} | n \rangle + O\left(\frac{1}{M^2}\right) \quad (17)$$

By evaluating each of the individual matrix elements, the partition function then becomes

$$Z = \lim_{M \rightarrow \infty} \left[ \frac{m}{2\pi\tau\hbar^2} \right]^{\frac{M}{2}} \int \prod_{i=1}^M (dx_i) \exp \left[ -\frac{\tau\hbar^2}{2m} \sum_{i=1}^M (x_{i+1} - x_i)^2 \right. \\ \left. - \tau \sum_{i=1}^M V(x_i) \right] \quad (18)$$

where

$$\tau = \frac{\beta}{M} \quad (19)$$

and

$$x_{M+1} = x_M \quad (20)$$

In particular, for a harmonic potential of the form

$$V(x) = \frac{1}{2} m \omega x^2 \quad (21)$$



the partition function in one dimension becomes

$$Z = \lim_{M \rightarrow \infty} \left[ \frac{m}{2\pi\tau\hbar^2} \right]^{\frac{M}{2}} \int \prod_{i=1}^M (dx_i) \exp \left[ -\frac{\tau\hbar^2}{2m} \sum_{i=0}^M (x_{i+1} - x_i)^2 - \frac{\tau m \omega^2}{2} \sum_{i=1}^M x_i^2 \right] \quad (22)$$

The evaluation of Eq(22) for the limit as M approaches infinity gives the same results as the evaluation using standard enumeration techniques of statistical mechanics.

A similar procedure is used for the 3-d fcc system to obtain the partition function and to calculate the zero pressure bulk modulus at various temperatures for a rare gas solid and then to compare with experimental results and other numerical techniques.

Generalizing the partition function to three dimensions requires an expansion of the Hamiltonian. The Hamiltonian in three dimension becomes

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad (23)$$

where

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k} \quad (24)$$

is the position of the particle. Similar to Eq.18 the partition function becomes

$$Z = \lim_{M \rightarrow \infty} \left[ \frac{m}{2\pi\tau\hbar^2} \right]^{\frac{3M}{2}} \int \int \int \prod_{i=1}^M (d\vec{r}_i) \exp \left[ -\frac{\tau\hbar^2}{2m} \sum_{i=1}^M |\vec{r}_{i+1} - \vec{r}_i|^2 \right. \\ \left. - \tau \sum_{i=1}^M V(\vec{r}_i) \right] \quad (25)$$

where

$$x_{M+1} = x_M \quad (26)$$

$$y_{M+1} = y_M \quad (27)$$

and

$$z_{M+1} = z_M \quad (28)$$

The potential that is used in the simulation of the quantum Monte Carlo method is the Lennard-Jones potential with nearest neighbor interactions. The Lennard-Jones potential has the form

$$\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (29)$$

From this potential and the use of the quantum Monte Carlo method, this thesis seeks to find the zero pressure bulk modulus at various temperatures.

The bulk modulus is defined as

$$M_B = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (30)$$

where  $P$  is the pressure and  $V$  is the volume. The volume is assumed to be cubic in nature, that is

$$V=r^3 \quad (31)$$

where  $r$  is defined as the lattice constant. The zero pressure bulk modulus then becomes

$$M_B = -r^3 \left( \frac{\partial P}{\partial r} \right)_T \left( \frac{\partial r}{\partial V} \right)_T \quad (32)$$

With

$$\frac{\partial V}{\partial r} = 3r^2 \quad (33)$$

the bulk modulus in its final form becomes

$$M_B = -\frac{r}{3} \left( \frac{\partial P}{\partial r} \right)_T \quad (34)$$

From the partition function the pressure can be found by

$$P = -\frac{1}{\beta} \frac{\partial}{\partial V} \ln Z \quad (35)$$

By entering both the temperature and the specific lattice constant of the quantum mechanical system, the pressure can then be found by implementing the quantum Monte Carlo method. By graphing the pressure versus lattice constant of the quantum mechanical system, and assuming a linear relationship between the pressure and the lattice constant of the system, the slope can then be found by using linear

regression techniques. The results of the quantum Monte Carlo method to determine the zero pressure bulk modulus of a rare gas solid will now be discussed.

## CHAPTER III

### RESULTS

A system of 108 atoms with nearest neighbor interaction governed by a Lennard-Jones pair potential was simulated. By entering the temperature and lattice constant of the system the pressure would be found. The zero pressure bulk modulus can then be found. Only nearest neighbor interactions were considered.

In solving for the zero pressure bulk modulus of a rare gas solid using the quantum Monte Carlo method, the Metropolis importance sampling was set at a 40 to 60 percent acceptance ratio. As explained previously, an acceptance is defined as the fraction of Monte Carlo steps used in averaging. Enough Monte Carlo steps are needed to bring the system into equilibrium before data is accumulated. A convergence of the system to equilibrium is required to get a realistic solution. The temperature is a key factor to the number of Monte Carlo steps needed. The higher the temperature is, more Monte Carlo steps are needed for convergence to equilibrium. In this thesis, at temperatures of 14.98K, 17.11K, 19.97K, 23.96K and 29.95K an  $M$  of 200 was used which resulted in 1,280,000 iterations used in computing averages, and at temperatures of 39.93K

and 59.90K, an M of 300 was used which resulted in 1,920,000 iterations to get the required number of Monte Carlo steps that were needed to compute the properties of the rare gas solid. The value of M was chosen to insure a reasonable degree of convergence. For the quantum Monte Carlo method there was a deviation of between .1% at low temperatures to 1% at the higher temperature runs. This deviation was due to the degree of convergence of the quantum Monte Carlo method. Though the quantum Monte Carlo method is superior to previous methods used as it treats both quantum and thermal effects in an essentially exact manner, the computer time required is quite large for the amount of data that was needed to find the zero pressure bulk modulus of a rare gas solid. For the number of iterations required to compute averages of the system, the total computer time took between 24 to 36 hours to get a single point. To speed up this time the computer program was parallelized so that many different points could be found in the same time frame as a single point could be found without parallelization. The parallelization was performed on an nCube computer that had the capacity to find 128 different points simultaneously.

## CHAPTER IV

### DISCUSSION

Graphs of the pressure versus lattice constant for each of the temperatures are shown in Figures 1-7. The crosses on the graphs represent the individual points from the quantum Monte Carlo method. The line on the graph represents the equation that best fits the points that are graphed. The percent error in the fitness of the line to the data varies approximately from 5% at the lower temperatures to as much as 50% at the highest temperature. The slope of the line is the value of the derivative in Eq. (34). The lattice constant when the pressure is zero can be read directly off the graph. With both of these values and Eq. (34) the zero pressure bulk modulus can be found.

Figure 8 is a graph of zero pressure bulk modulus versus temperature as found from the quantum Monte Carlo method described previously and a graph from Klein and Venables (1976) of zero pressure bulk modulus versus temperature of argon found from experimental methods. It should be noted that at the higher temperatures there is a larger margin of error than at lower temperatures. The graph of argon is being used to compare with the results of the quantum Monte Carlo method because it is a common rare

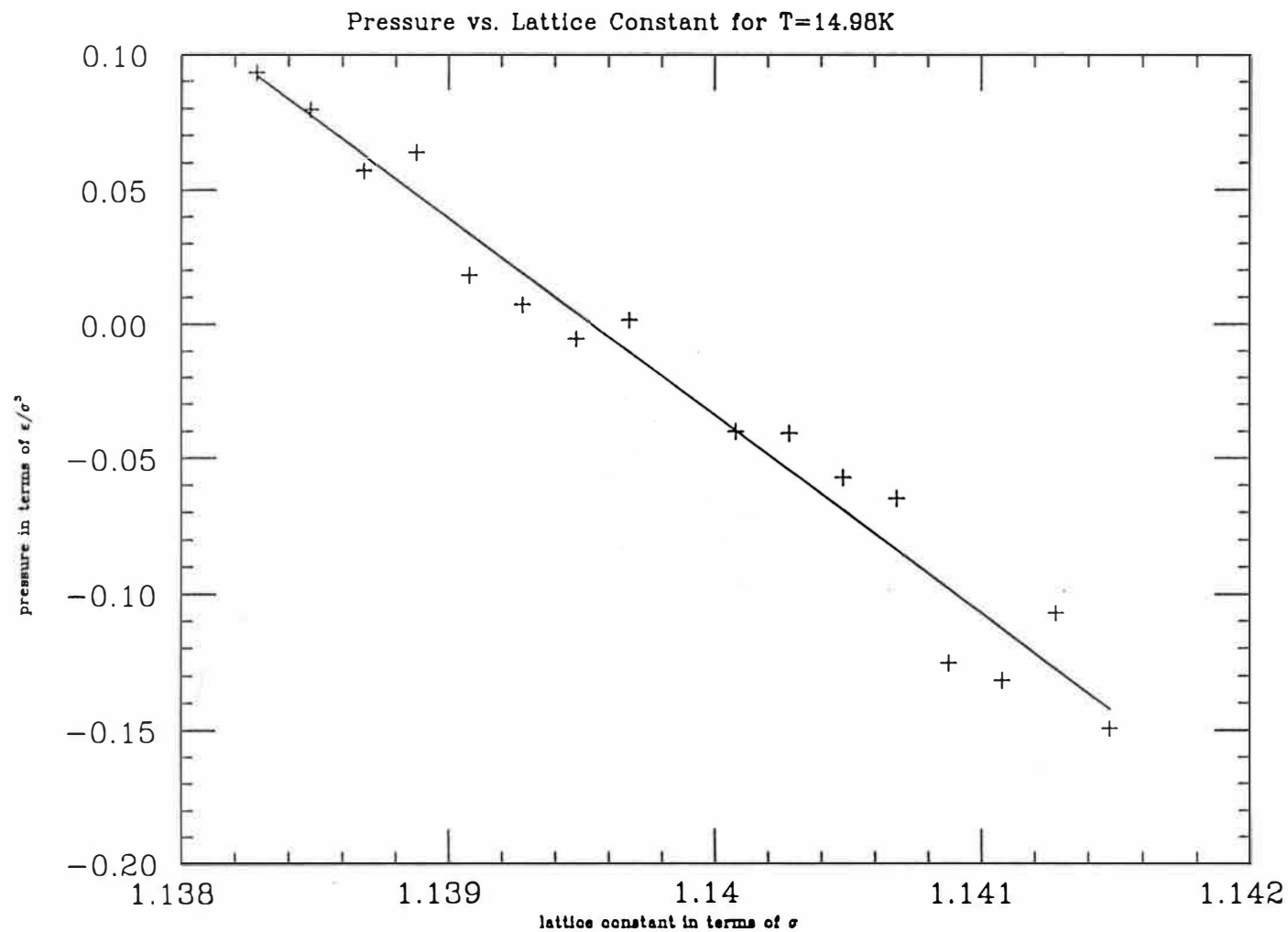


Figure 1. Graph of Pressure Versus Lattice Constant for a Temperature of 14.98K.



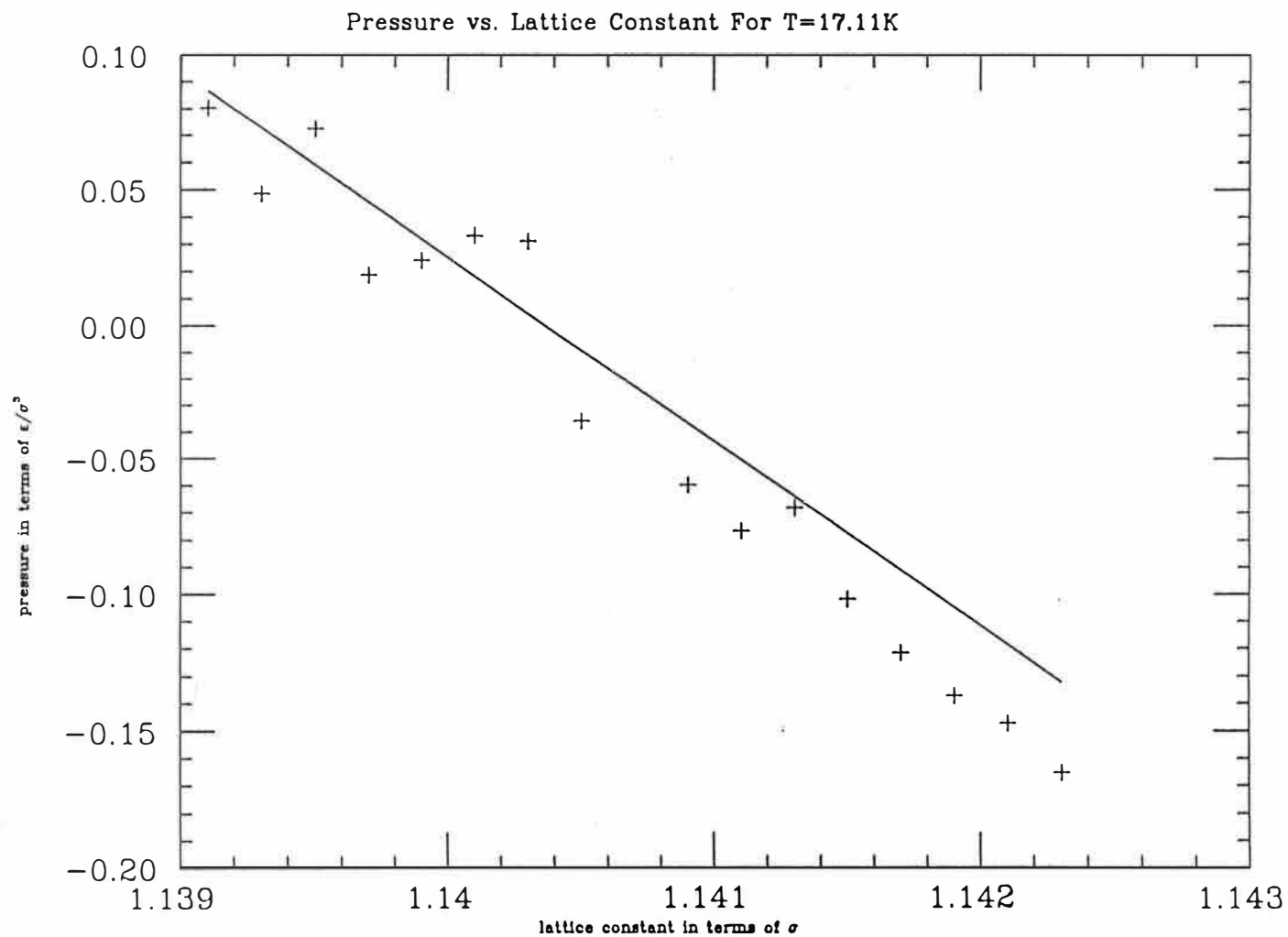


Figure 2. Graph of Pressure Versus Lattice Constant for a Temperature of 17.11K.

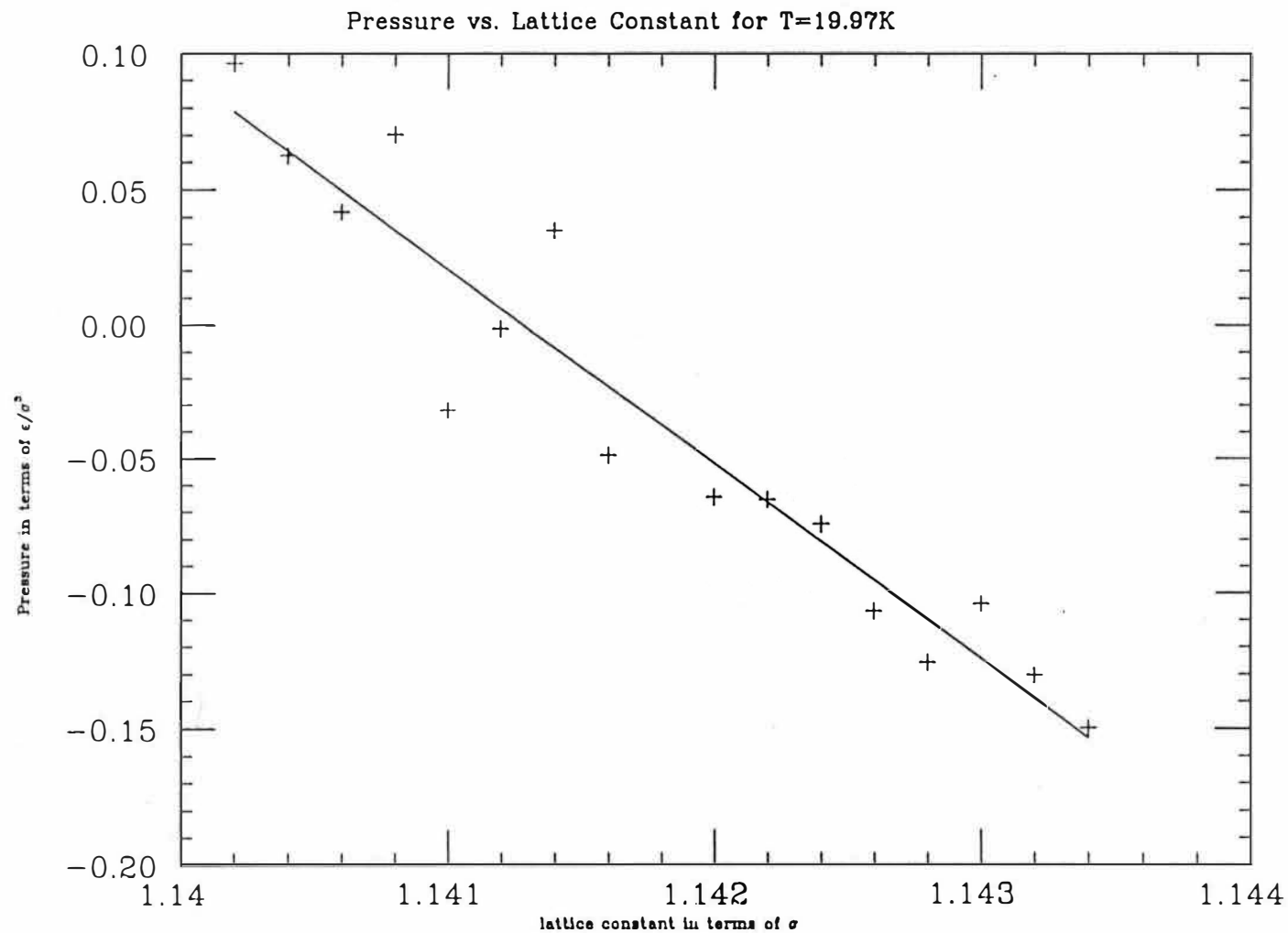


Figure 3. Graph of Pressure Versus Lattice Constant for a Temperature of 19.97K.

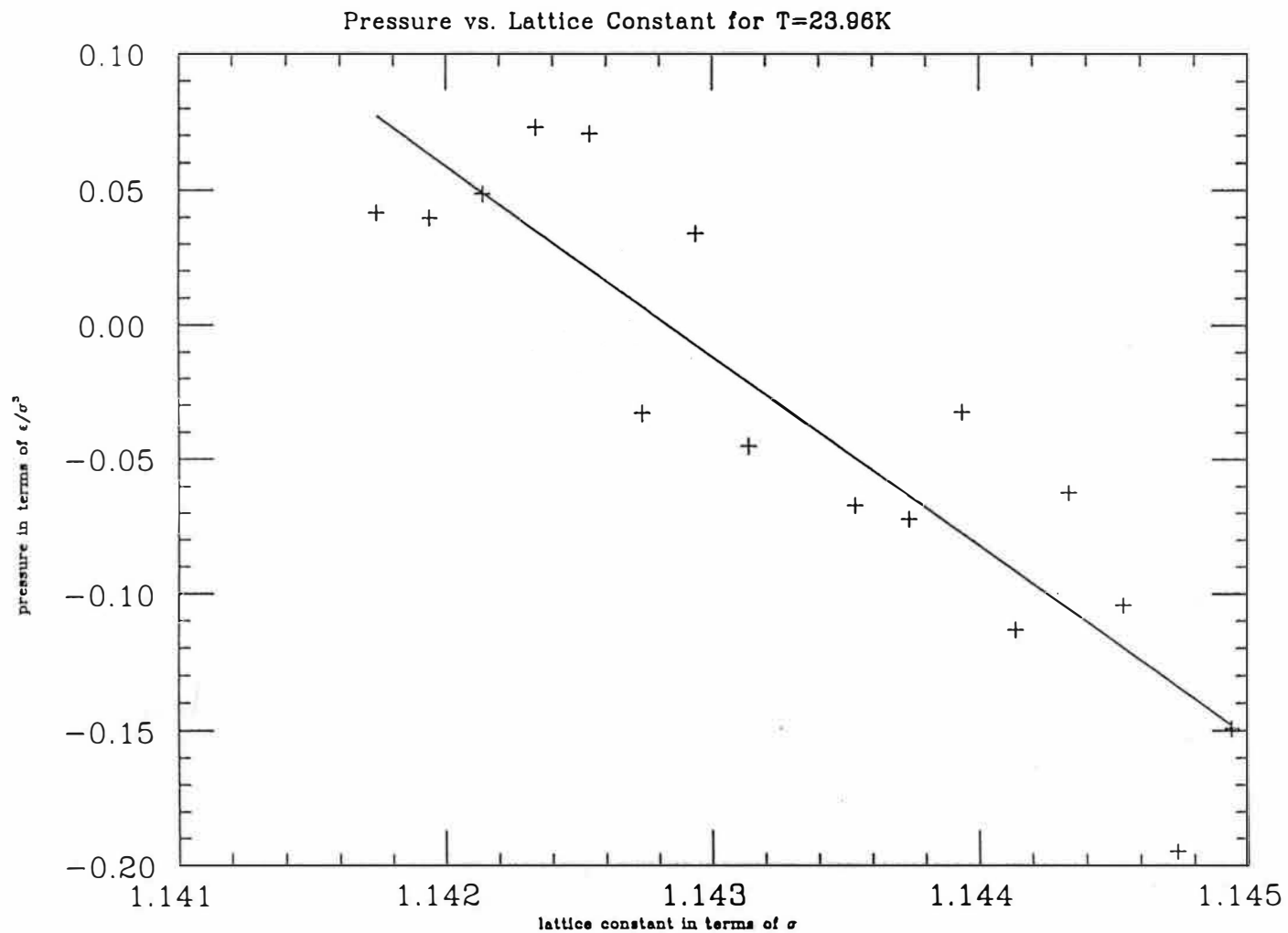


Figure 4. Graph of Pressure Versus Lattice Constant for a Temperature of 23.96K.

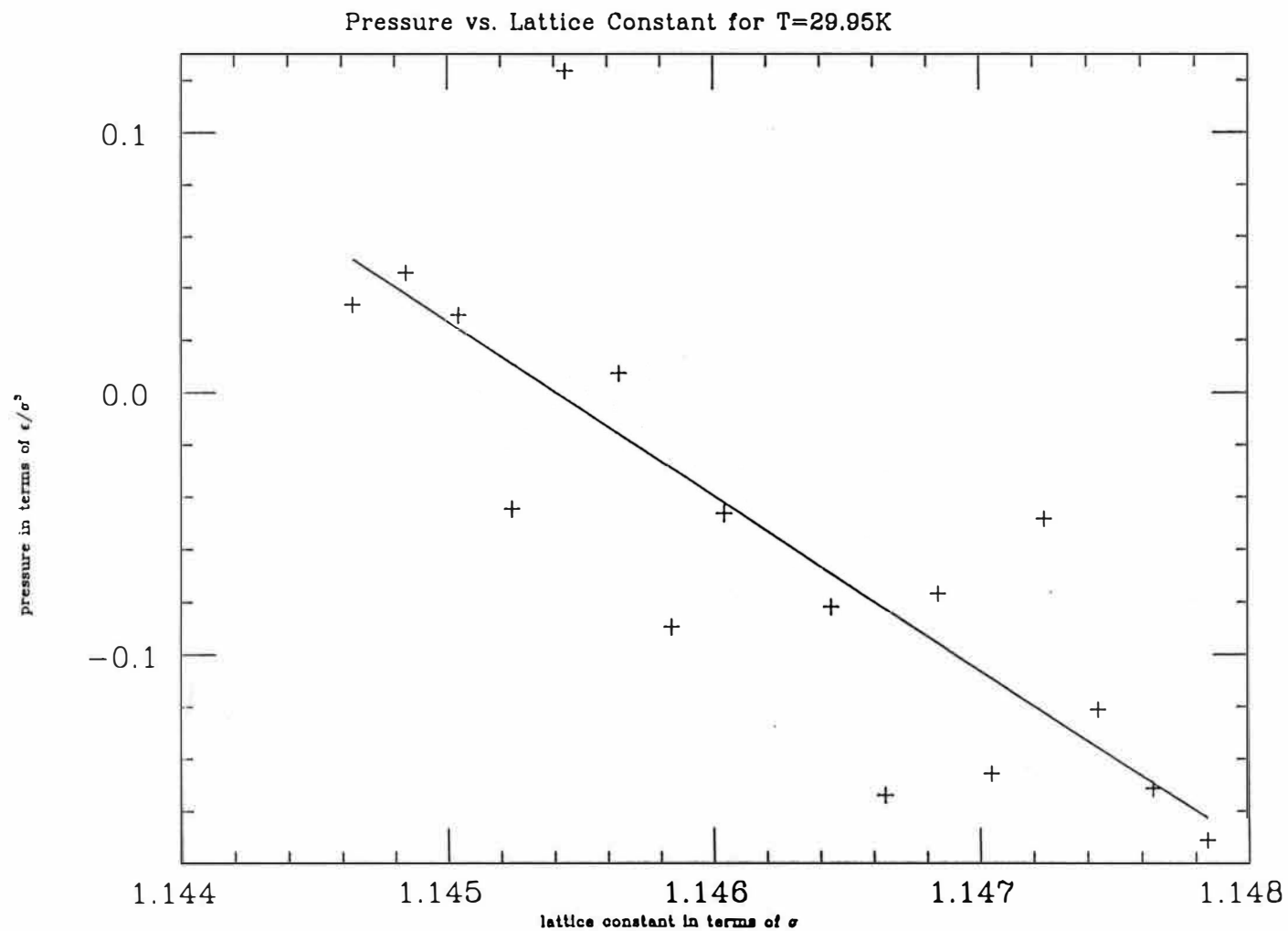


Figure 5. Graph of Pressure Versus Lattice Constant for a Temperature of 29.95K.

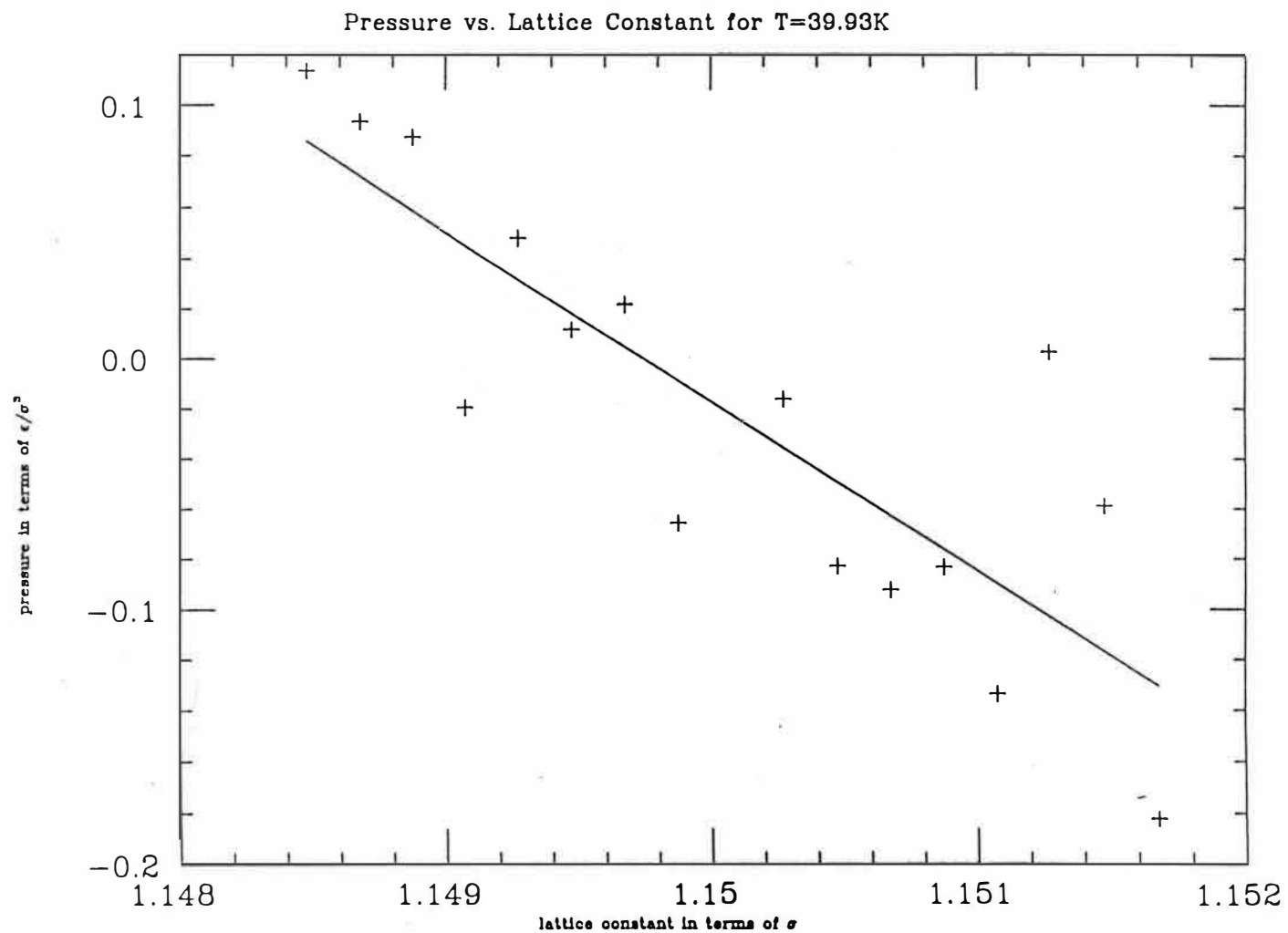


Figure 6. Graph of Pressure Versus Lattice Constant for a Temperature of 39.93K.

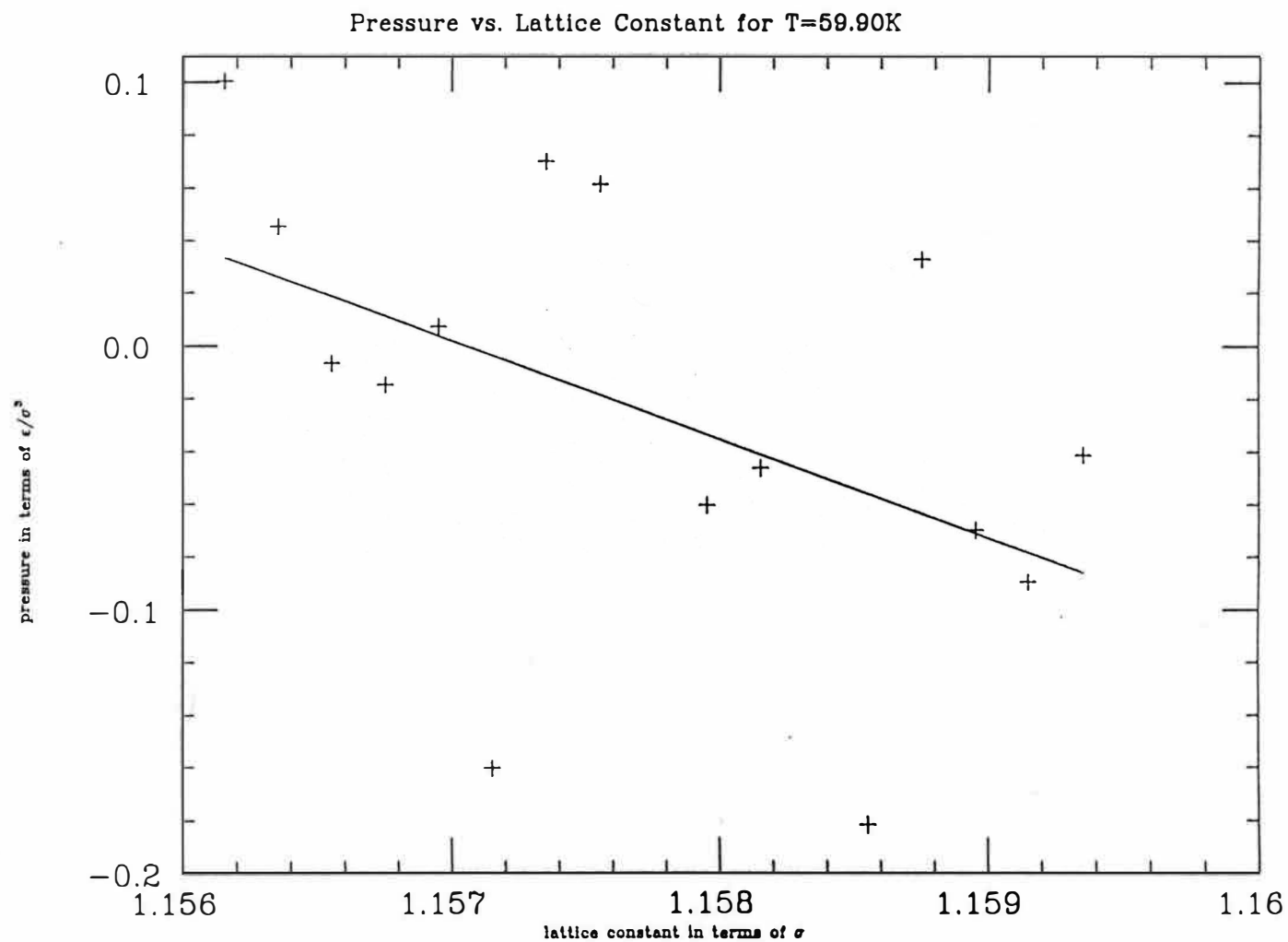


Figure 7. Graph of Pressure Versus Lattice Constant for a Temperature of 59.90K.

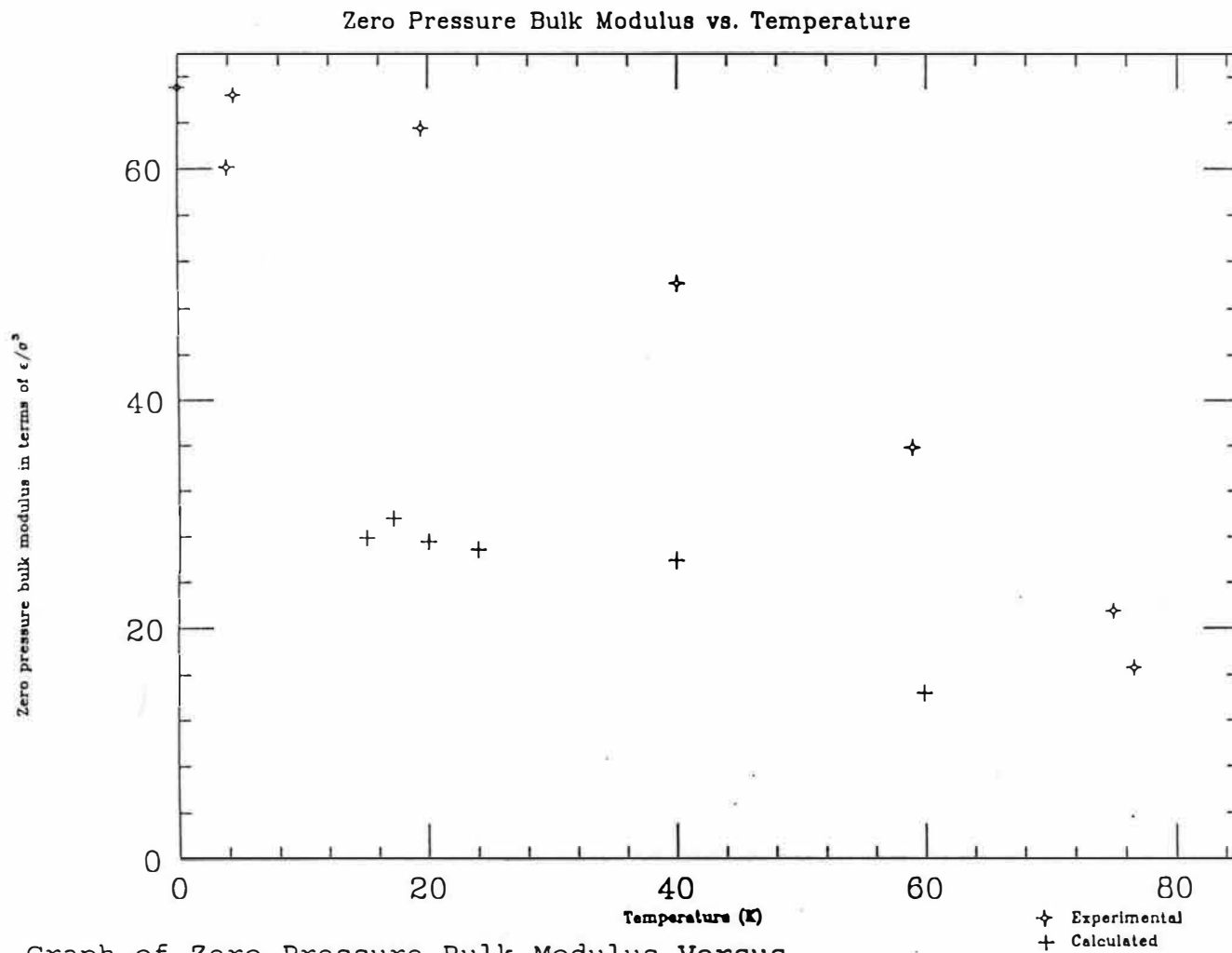


Figure 8. Graph of Zero Pressure Bulk Modulus Versus Temperature for Experimental and Calculated Results.

gas that can be described by a Lennard-Jones potential. For an accurate Lennard-Jones modeling, however, more than just nearest neighbor interactions are needed. We do not expect great accuracy in our comparison because of this.

As can be seen from figure 8, the same generalized curve is observed. However the calculated values shown are reduced by approximately a factor of two compared to those arrived at experimentally. This discrepancy in the values will now be discussed.

In the quantum Monte Carlo calculation of the zero pressure bulk modulus of a rare gas solid only nearest neighbor interactions of the Lennard-Jones potential were used. Most treatments by other methods use many more neighbors. A classical treatment of the zero pressure bulk modulus of a Lennard-Jones potential at 0K by Kittel (1976) with infinite neighbor interactions ( $M_B = 75.32\epsilon/\sigma^3$ ) was found to be approximately twice the value obtained from the  $T=0K$  classical method when considering only nearest neighbor interactions ( $M_B = 48.0\epsilon/\sigma^3$ ). This result indicates that the major discrepancy between the quantum Monte Carlo method and experimental data arise from the restrictions to nearest neighbor forces.

We conclude that, a further study of the quantum Monte Carlo method is needed that includes longer range interactions of the Lennard-Jones potential for a more successful



comparison with experimental data.

## REFERENCES

- Barma, M and Shastry, B. S., Phys. Rev. B 18, 3351 (1978)
- Ceperley, D. M. and Pollock, E. L., Phys. Rev. Lett. 56, 351 (1986).
- Ceperley, D. M. and Jacucci, G. Phys. Rev. Lett. 58, 1648 (1987).
- Hirsch, J. E., Scalapino, D. J., Sugar, R. L., Blankenbecler, R., Phys. Rev. Lett. 47, 1628 (1981).
- Hirsch, J. E., Sugar, R. L., Scalapino, D. J., Blankenbecler, R., Phys. Rev. B 26, 5033 (1982).
- Klein, M. L., Venables, J.A., Rare Gas Solids, vol. 1 (Academic Press, New York, 1976).
- Kittel, C., Solid State Physics, (Wiley, New York, 1976).
- Suzuki, M., Commun. Math. Phys. 51, 183 (1976).
- Suzuki, M., Prog. of Theor. Phys. 56, 1454 (1976).