California Institute of Technology

EQUATION OF STATE FOR POLYMETHYLMETHACRYLATE (PMMA)

A dissertation submitted to
the Faculty of the Division of Mathematics, Physics and Astronomy
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BY
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To my parents.

ABSTRACT

With ever-increasing computing power, simulations of larger, more complex systems are becoming more and more feasible. The ability to model systems, especially those not easily studied in the laboratory, is desired. But with these strictly computational problem there comes a question of accuracy. In this paper, a well-studied polymer, polymethylmethacrylate (PMMA), will verify the computational results obtained for polymers which are less easily (if at all) studied experimentally. Assuming that a small sample accurately represents the system as a whole, energy calculations with the simulation engine Cerius2 will be used to determine a cold compression curve, followed by a series of molecular dynamics calculations to determine the Grüneisen parameter. These calculations may be compared with the ample experimental evidence available for PMMA, providing a calibration for those substances (such as Kel-F) which cannot be studied experimentally. Further basis for comparision can be obtained using various viscoelastic and thermodynamic properties. Additionally, the Grüneisen parameter may be used to revese the traditional experimental approach to calculate the Hugoniot data, providing further basis for comparision and an opportunity for improving the accuracy of the model.

ACKNOWLEDGEMENTS

I’d like to thank my advisors, Dr. William A. Goddard, III, and Dr. Gregg Caldwell, for timely advice guidance and the occasional ”Hey, are you still alive?” email. In addition, the computation and analysis would have taken a lot longer without the WAG group and the Caltech ASCI group. Deserving of particular recognition are Dr. Goddard’s 5 secretaries, who have helped with everything from getting SURF paychecks to finally sending that graduate school recommendation out over the last 2.5 years.

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CHAPTER 1

INTRODUCTION

In the last twenty years, computing power has grown to allow modeling of extremely complex systems, creating strides in pharmaceutical development and protein folding. These advances can also be applied to non-biological situations. Careful creation of a model combined with equally thoughtful choice of a force field can produce accurate simulations for these complex systems.

This study attempts to evaluate one such material, the polymer polymethylmethacrylate (PMMA), through a specially optimized model space and the more standard exponential-6 force field. Data from these calculations are used to develop a cold compression curve. Using this as a starting place, additional molecular dynamics calculations provide data points to fit to the Mie-Grüneisen Equation of State, which leads to a calculation of the Grüneisen parameter, $G(V, T)$.

PMMA is also well-studied experimentally, providing a basis for the accuracy of computational studies. The computational value of G can be compared to values obtained in lab from experimental determination of the Hugoniot. Since this calculation is virtually unbiased by systematic laboratory error, a good comparision can be made by reversing this lab technique and calculating the Hugoniot equations from the Grüneisen parameter.

The design of numerical engineering models for high explosives involves the development of approximated and exact solvers for the Euler equations governed by high explosive equations of state. This Mie-Grüneisen Equate of State will contribute to this goal by providing a connection between the computational calculations and the experimental data.

To calculate an Equation of State by any method requires not only algorithms but also an understanding of the thermodynamic background. Although the theoretical formulas are simple, the calculations are not. These calculations combine theory from almost every aspect of physics. The force field is a purely classical entity, while the velocity auto correlation depends on both statistical and quantum mechanics.

CHAPTER 2
THERMODYNAMICS

2.1 Mie-Grüneisen Equation of State

For this calculation, the data generated was fit to the Mie-Grünheisen Equation of State by assuming a temperature T = 0 K, varying the volume V (and thus the pressure P) of the system, and finding the minimum energy E for that case.

$$P(V) = P_o + \frac{G(V,T)}{V}[E(V) - E_o]$$

P_o and E_o are determined by this equation, in addition to the Grüneisen parameter G(V,0) for this specific case. This equation of state is intended for the reactants of a mixture.

2.2 Cold Compression Curve

The calculation began by detmining the cold compression curve, or the relationship betwen pressure, energy and volume at fixed temperature T= 0 K. This provides values E_o and V_o for later calculations.

2.3 Grüneisen Parameter

The Grüneisen parameter, $G(V,T)$ is defined as:

$$G(V,T) = \frac{\partial E}{\partial P},$$

which can be considered as:

$$\begin{aligned} G(V,T) &= \frac{\frac{\partial E}{\partial T}}{\frac{\partial P}{\partial T}} \\ &= \left(\frac{\partial E}{\partial P}\right)_V \end{aligned}$$

2.4 The Hugoniot Equation

The Hugoniot equations are used to describe the behavior of a material through which a shock wave has passed. These equations link the pressure P, internal energy E, and density ρ in front of a shock wave (uncompressed: P_o, E_o, ρ_o) to values after the shock front has passed (compressed: P, E, ρ). The density is expressed as the specific volumes $V = 1/\rho$ and $V_o = 1/\rho_o$ for the compressed and uncompressed cases, respectively. In a laboratory experiment, initial pressure, energy, and density before the shock are known values, while the respective values after the shock are unknown quantities, as are the shock velocity U and particle velocity u_p behind the shock front. The Hugoniot equations are then written as:

$$\begin{aligned} \rho(U - u_p) &= \rho_o U \\ P - P_o &= \rho_o u_p U \\ E - E_o &= (P + P_o)(V_o - V)/2 \end{aligned}$$

$E - E_o$ can also be determined from the Mie-Grüneisen equation:

$$E - E_o = V(P - P_o)/G$$

Experimentalists frequently use Hugoniot curves to determine the Equation of State. In this case, the Equation of state eventually will be used to compute the Hugoniot curves.

CHAPTER 3
MODELING METHODS

Any classical computational simulation of discrete bodies consists of two parts: the model and the force field. The model contains position, mass, charge, and other fundamental qualities of the atoms being modeled. The force field describes their motion due to one another's influence, or due to the influence of external conditions such as temperature and pressure.

3.1 The Model

The model in this case was built using an algorithm developed by Mario Blanco of the MSC which produces a randomly-distributed sample with the correct density. Initially, the only data given to the computer are the atomic charges, the sizes of the atoms and their masses. Then, polymer chains are assembled from these elements (H, C, O in the case of PMMA) under periodic boundary conditions.

The building algorithm starts with one-half of the required density, runs a simple minimization to find the lowest energy configuration of the system, and performs a brief NVT (constant-volume, constant-temperature) molecular dynamics calcuation. These two steps are repeated until the experimental density is reached. The NVT calculation intoduces a random element into the sample, so that no two samples generated by this algorithm will be the same.

Since micromodeling techniques are being used to describe macroscopic quantities of material, this variation between "samples" is important. A more complete calculation than that presented here would cover several such models. Unfortunately, computer speed and hard drive size limited the scope of this calculation.

3.2 The Force Field

If the model represents the ingredients of a recipe, the force field is the directions. The force field specifies functional forms of components of the energy expression, parameters for the fuctional forms and instructions for assigning functional forms and parameters. In other words, the total energy of the system is expressed as combination of terms such as hydrogen bonding, torsional energy, van der Waals forces, etc.

There are numerous advantages to classical forcefield-based calculations. Forcefield-based simulations can handle larger systems more quickly than equivalent quantum calculations. In addition, forcefield calculations can be broken down into component energy, providing a wider scope of analysis. For example, a calculation can target torsional energy or non-bond energies, a distinction that is not always easy to make in quantum simulation engines. Finally, because the forcefield is specifed by these components, constraints are easily imposed on the system: atoms can be locked into place, energies can be directed towards a certain value.

A well-chosen forcefield will describe entire classes of molecules with reasonable accuracy. Some forcefields, such as the Universal Force Field (UFF), cover the entire periodic table with lower accuaracy than those designed for a smaller set of atomic types.

3.2.1 Choosing a Force Field

For this calculation, the Dreidung-exponential 6 Force Field (exp6) was used. Exp6 was developed at the MSC, and is intended for use with plastics. The general formula is:

$$\begin{aligned} U_{total} &= \sum_{molecule} (E_d + E_{nd}) \\ &= \sum_{molecule} (E_b + E_\theta + E_\phi + E_{inv} + E_{nb} + E_\varepsilon + E_{hb}) \end{aligned}$$

Each of these E terms or functional forms calculates a specific type of energy, as defined below.

3.2.2 The Chemical Bonding Functional

The bonding energy is given by:

$$E_b = \frac{1}{2}k_b(r_{ij} - r_o)^2,$$

where r is the distance between bonding atoms, k_b is a constant and r_0 is the minimum distance allowable. This term determines the energy between bonded atoms i and j. It can also be thought of as a stretching energy term. Unlike the Morse term, this harmonic potential does not allow unrealistic bondlengths.

3.2.3 The Valence Angle Functional

The energy in a specific angular configuration is given by:

$$E_\theta = \frac{1}{2}k_\theta(\theta_{ijk} - \theta_0)^2,$$

where θ_0 is the angle of minimum energy and k_θ is a constant. This term gives the energy of a certain angle between three atoms i, j, k, which are not necessarily bonded.

3.2.4 The Torsion Functional

The torsional energy, the energy in planar angles of clusters of atoms, is given by:

$$E_\varphi = \frac{1}{2}k_\varphi(1 + cos(m(\varphi_{ijkl} + \varphi_{offset}))),$$

where φ_{offset} is the minimum energy planar configuration of atoms i, j, k and l and k_φ is a constant.

3.2.5 The Inversion Functional

Inversion energy, or the energy of out of plane torsions is given by:

$$E_{inv} = \tfrac{1}{2} K_{inv} (\psi - \psi_0)^2,$$

where K_{inv} is a constant, and ψ_0 is a minimum configuration.

3.2.6 The van der Waals Functional

The interactions between atoms i and j at large distances, i.e., non-bonded atoms, or van der Waals forces, are given by:

$$E_{nb} = Ae^{-Bd_{ij}} - Cd_{ij}^{-6},$$

a modified Lennard-Jones potential. This van der Waals term is the key motivation behind use of this force field. Unlike a Dreidung-Lennard-Jones force field, this van der Waals term has a gentle ascent, which creates a more accurate simulation of close-packed atoms.

3.2.7 The Couloumb Functional

The charge of the atom is considered in this functional,

$$E_\epsilon = \tfrac{q_i q_j}{\epsilon d_{ij}},$$

for the electrostic interactions between atoms i and j, with charges q and separating distance d_{ij}.

3.2.8 The Hydrogen Bond Functional

Finally, a special term is used to describe the Hydrogen Bonds in this simulation:

$$E_{hb} = \tfrac{F}{d_{ij}^{12}} - \tfrac{G}{d_{ij}^{10}}.$$

This augments the electrostatic description of the hydrogen bond.

3.3 Minimization

In order to obtain the initial structures it is neccessary to calculate the cold compression curve, which requires minimizing the energy of the system. Throughout the molecular dynamics calculation, the default smart minimization algorithm of Cerius2 is used or slightly reorder the atoms and mimic actual time evolution. It combines Steepest Descent, ABNR Newton, Quasi-Newton and Truncated Newton methods to obtain the system of minimum energy. This is the most effcient method in terms of computation time available for this simulation engine at this time.

3.3.1 Steepest Descent Method

A line search changes the atomic coordinates to a new lower-energy structure. Essentially, it consists of a one-dimensional minimization along a vector determined at each iteration. Extensive line searches are inefficent for locating the minimum energy precisely, but they allow rapid progress towards the minimum. A Steepest Descent search, the first step in the smart minimizer, is a line search along the direction of the local downhill gradient. Eachline search produce a direction perpendicular to the previos gradient, but the directions oscillate towards the minimum.

3.3.2 Adopted Basis Newton-Raphson Method

The Adopted Basis Newton-Raphson Method (ABNR) is designed to take advantage of the accurate Newton-Raphson Method without the large storage requirements of that method.

The general steps of any Newton-Raphson method are:

- Supply an initial guess r_o.
- Test for convergence.
- Compute an *approximate* Hessian A that is positive definite.
- Solve for the search direction p_k such that

$$\| A_k p_k + g_k \| < \varphi_k \| g_k \|$$

where φ_k is some prescribed quantity that controls the accuracy of the computed p_k.

- Compute an appropriate step length λ_k so that the energy decreases by a sufficient amount.
- Increment the coordinates:

$$x_{k+1} = x_k + \lambda_k p_k$$

- Go to the second step.

This method avoids the intensive memory requirements of the pure Newton-Raphson method by constructing the second derivative matrix from the change in the gradient vectors, and has a special routine to identify and avoid saddle points in the energy equation. It has a linear convergence.

3.3.3 Quasi-Newton Method

The quasi-Newton-Raphson method also uses the gradients of previous iterations to direct the minimization along an efficient pathway. Instead of calculating the Hessian, it uses a matrix which approximates the inverse of the Hessian in the limit of convergence. this matrix is also always positive-defined and symmetric, so successive steps always minimize the energy. This method is very inefficient in areas of rapidly-changing gradient.

3.3.4 Truncated Newton-Raphson Method

Finally, to obtain the most precise minimization, the Truncated Newton-Raphson Method is utilized. It is memory-intensive, as it actually calcuates the second derivatives to generate the Hessian. This makes it more stable than previously discussed methods. In addition, tolerance for convergence is dependent on proximity to the minimum. It is more efficient to begin with many poorly-defined Newton steps than to take fewer well-defined steps, because convergence improves as you approach the minimum value.

3.4 Molecular Dynamics

Molecular dynamics (MD) calculations solve the classical equations of motion for an N-atom system, with atomic interactions dictated by the forcefield. These simulations are useful when studying the time evolution of a system at a non-zero temperature. In this case, the MD calculations generate a statistical ensemble from which various thermodynamics properties can be calculated.

Molecular dynamics typically is concerned with solving the familiar:

$$F_i(t) = m_i a_i(t)$$

The force on an atom can be computed directly from the derivative of the potential energy (as specified int he force field).

$$\frac{\partial V}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t_i^2}$$

The coordinates and velocities of any atom in the system can be determined for any subsequent time. A trajectory is the complete record for the entire dynamics run.

Cerius2 uses the Verlet leapfrog algorithm to integrate the equations of motion. It requires modest computations, modest memory and allows a large timestep.

3.4.1 NVT dynamics

Ideally, the simulation would be carried out as a constant temperature, constant pressure (NPT) ensemble, which most resembles laboratory conditions. However, this is unfeasible due to the non-periodic nature of the model, and computational limits. Instead, the constant-temperature, constant-volume ensemble is employed. By considering a series of volumes, calculations for $\partial E/\partial T$ and $\partial P/\partial T$ can be made, resulting in an accurate computation with less strain on the computing resources.

Dynamics simulations normally have 2 stages, equilibration and data collection. In the initial equilibriation stage, velocities are randomly assigned to the component atoms, according to the Maxwell-Boltzman distribution about the desired temperature. Convergence is highly dependent on the simulation, the force field and the model.

3.4.2 Nosé-Hoover Thermostat

In order to control the temperature of the simulation a thermostat is needed. In Cerius2, there are several options, including Nosé-Hoover.

Nosé-Hoover dynamics produces true canonical ensembles in both coordinate space and in momentum space. A fictitious degree of freedom is added to the system under consideration to represent the system's interaction with the heat bath. These new equations of mass are solved, and if the forcefield is correct, the constant-energy dynamics (NVE) will produce the canonical ensemble (NVT) of the real system. Because the Nosé-Hoover method produces evenly spaced trajectory points, it is useful for studies which will involve autocorrelation.

3.5 Quantum Correction

Force fields are an entirely mechanical approach to predicting the behavior of large systems. Because forcefields are based on observations, quantum effects are empirically included. This means that the forcefield approach is limited—for example, acid/base reactions are not easily modeled using this method. While simulations have the advantage of being free of laboratory bias, they can suffer from forcefield bias.

For some calculations, it is possible to calculate the quantum effects on the energy calculations. A technique has been derived from spectral analysis of the trajectory. The correction is based on the approximation that anharmonicities mainly affect the lower frequencies of the power spectrum, where the system behaves almost perfectly classically. Meanwhile, the higher frequencies, where the deviation from classical mechanics is greatest, have suffciently harmonic atomic motions that harmonic quantum corrections apply.

CHAPTER 4

CALCULATIONS AND CONCLUSIONS

Polymethylmethacrylate (PMMA) is a polymer, of density 1.06 g/cc. This model began at initial coditions, T = 0 K, P = 0 GPa, N = 1452 atoms (780 H, 480 C, 192 O). The initial unit cell was 24.16Å x 24.53Å x 25.28Å. Throughout all calculations, N, the number of atoms, remained constant.

4.1 Cold Compression

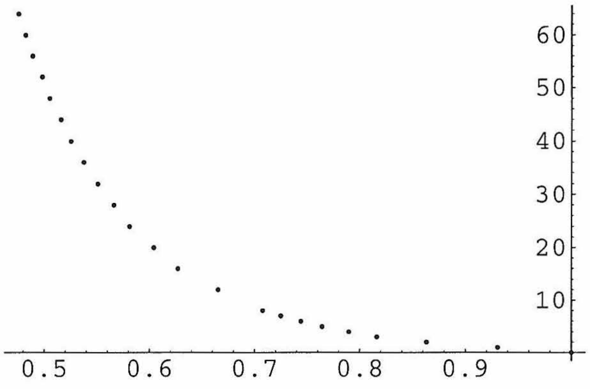
For the cold compression curve, minimized energies were recorded at P = 0-8GPa, and every 4 GPa after that to 64GPa.

Pressure, GPa	Volume/SV	Energy Kj/mol
0	15104.7	26572.7
1	14054.8	35321.5
2	13038.2	43325.1
3	12327.5	50734.3
4	11926.1	57850.5
5	11542.2	64673.7
6	11237.8	71287.6
7	10949.4	77734.0
8	10689.6	84013.0
12	10048.0	83845.6
16	9470.75	108543
20	9123.35	131733
24	8775.08	153542
28	8549.55	174598
32	8319.21	194984
36	8117.70	214909
40	7934.44	234374
44	7790.00	253337
48	7627.76	271964
52	7521.07	290257
56	7383.58	308257
60	7281.86	325964
64	7180.95	343545

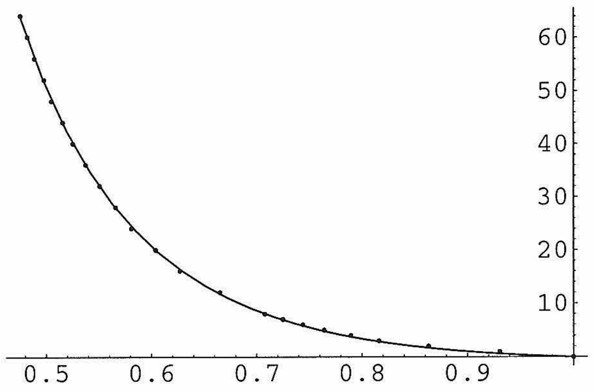
Table 4.1: Cold Compression Curve Data

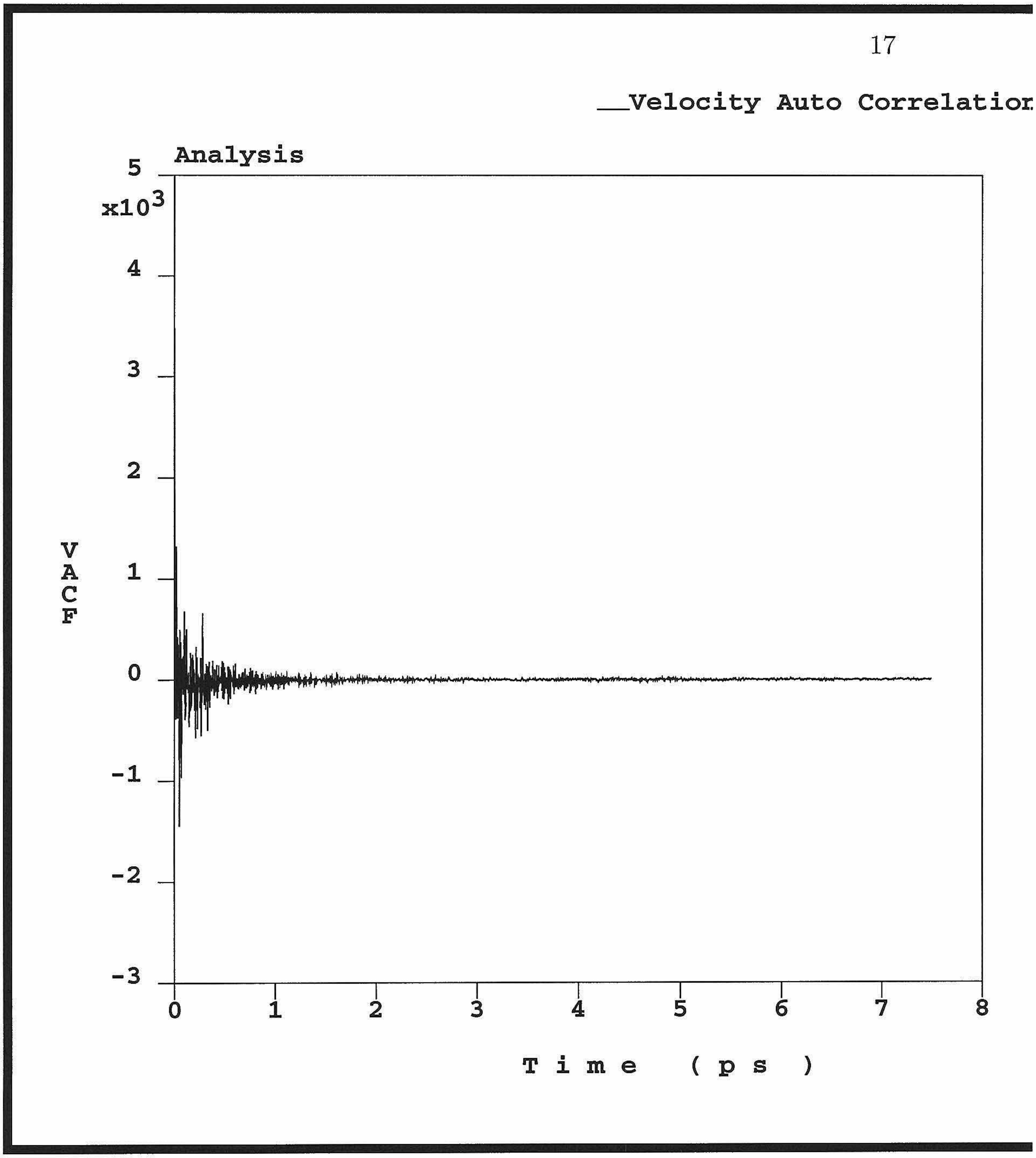
Cold Compression Data

pmmaEOS2.nb



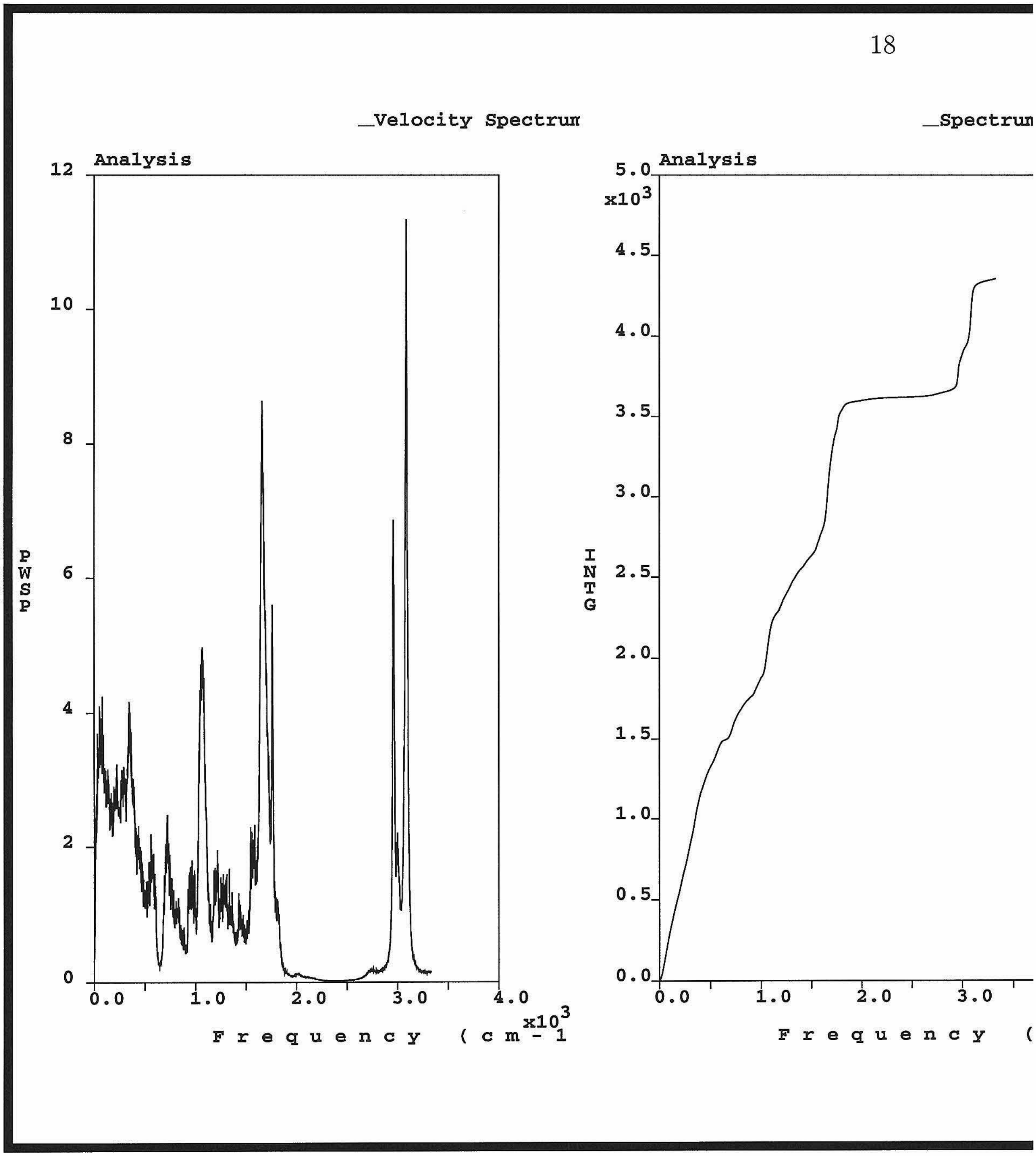
Cold Compression Fit–Birch Munagham





Convergence of .7 V/V_o, 500 K calculation

Clearly visible in this typical calculation is the initial equilibration, followed by rapid convergence.

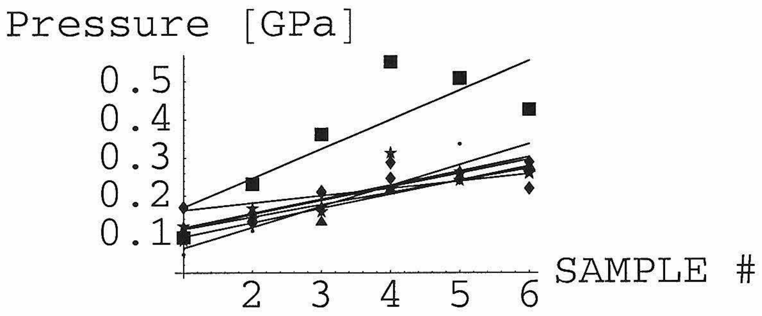


Power Spectrum of .7 V/V_o, 500 K calculation

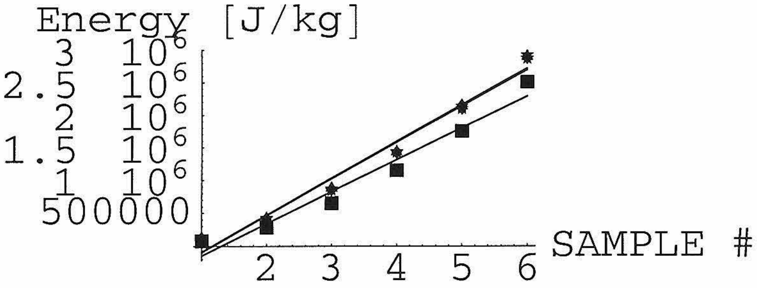
Clearly visble are the two peaks: one high frequency, one low frequency.

NVT dynamics trajectories using Nosé-Hoover thermostat were calculated for 6 volumes over 100-700K. To equilibrate, the simulation ran for 5ps without writing a trajectory, and for 15ps with a trajectory, allowing ample time for convergence. To take advantage of this accuracy, the pressure was obtained by averaging the running average pressure over the last 5 ps of the simulation.

Pressure-Volume Isotherms for PMMA



Energy-Volume Isotherms for PMMA



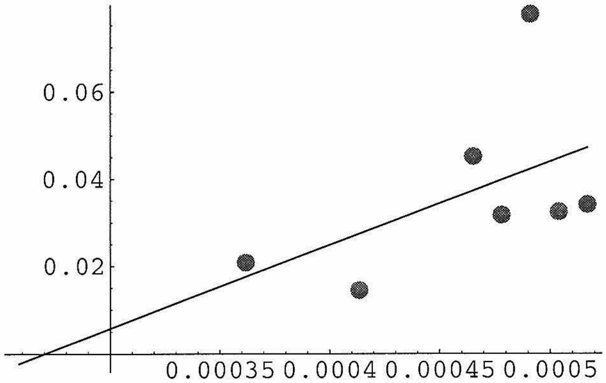
4.2 Conclusions

At present, the data for the PV iso therms and the EV isotherms seems a bit messy. The linear fit to obtain the Grüneisen is neccessarily inaccurate, since the Grüneisen parameter changes with the viscoelasticity of the material. At present, the nature of this dependence is not understood well enough to accurately model the effects.

$G_{coeff} = -0.0516948 + 0.0989553X$

Preliminary linear fit for the Grüneisen Parameter of PMMA

pmmaEOS2.nb

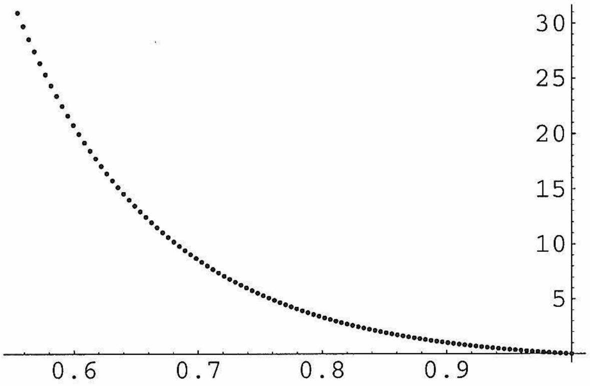


4.3 Further Work

Obviously, all of these numbers need to be compared to experimentally determined numbers. In addition, if this is a correct equation of state for PMMA, it should be possible to accurately compare the Hugoniot curve and other thermodynamic properties.

Hugoniot Curve obtained from calculated G(V,T)

pmmaEOS2.nb



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