

THERMODYNAMIC AND ELASTIC PROPERTIES OF POLYETHYLENE AT ELEVATED TEMPERATURES

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ABSTRACT

Over the years molecular modeling techniques, such as Molecular Mechanics, Monte Carlo and Molecular Dynamics have been applied to study the equilibrium thermodynamic and mechanical properties of materials. The accuracy of the predictions made by these techniques strongly depend on the force fields employed to represent the interactions in the studied system. Recently developed force field parameters for crystalline polyethylene are shown to reproduce the mechanical properties of polyethylene accurately through molecular mechanics. Here, we will present the statistical fluctuation formulae for the elevated temperature equilibrium thermodynamic and elastic properties in terms of microscopic variables such as energy, enthalpy, pressure, volume, microscopic strain or stress tensors and present preliminary results of our calculations.

INTRODUCTION

In molecular modeling of polymers and materials accurate prediction of properties and identifying the relevant structure - property relations are of utmost importance. Given a classical interaction force field, thermodynamic and mechanical properties of materials can be determined from molecular level interactions by harmonic theory, molecular mechanics or by molecular dynamics and Monte Carlo simulations. In the harmonic approximation or in molecular mechanics thermal contributions are introduced indirectly and the anharmonic contributions are neglected. In contrast, by accounting the thermal and anharmonic effects exactly, molecular dynamics and Monte Carlo methods through the use of the statistical mechanical fluctuation expressions for thermodynamic and mechanical properties provide accurate results within the validity of used force fields and classical mechanics.

In recent years molecular dynamics methods were extended to treat anisotropic systems [1-2] and were used efficiently in calculating elastic and thermodynamic properties of different solids at elevated temperatures [3-4]. In the next section, we will describe extended system molecular dynamics methods for anisotropic solids and summarize how the theory of finite elasticity is applied in computer simulations of materials.

MOLECULAR DYNAMICS OF ANISOTROPIC SOLIDS

In molecular dynamics, one solves equations of motion for a many body system to obtain the phase space trajectory of the system. Then, the physical properties, such as energy, pressure, stresses, etc. can be calculated as time averages over the trajectory. Furthermore, the response functions: specific heats, thermal expansion, compressibility, elastic moduli can be

obtained using the statistical mechanical fluctuation expressions. In this section, we describe the isothermal isotension (TtN) form of molecular dynamics method and present the fluctuation expressions for the thermodynamic and elastic properties of materials.

The extended Hamiltonian for TtN dynamics is

$$H(\rho_a, \pi_a, \mathbf{H}, P_H, s, P_s) = \sum_{a=1}^N \frac{\pi_a \mathbf{G}^{-1} \pi_a}{2m_a s^2} + U(\{\rho_a\}, \mathbf{H}) + \frac{P^2 \mathbf{H}}{2W} + V_0 \text{Tr}(\mathbf{t} \boldsymbol{\epsilon}) + \frac{P^2}{2Q} + (3N+1) k_B T_0 \ln(s) \quad 2.1$$

where (ρ, π) are the scaled coordinates and momenta of an atom, (\mathbf{H}, P_H) are the shape and size matrix and corresponding momenta and (s, P_s) are the Nose thermostat variables. Q and W are adjustable mass like variables for thermostat and piston variables. T_0 is the bath temperature and \mathbf{t} is thermodynamic tension and $\boldsymbol{\epsilon}$ is the strain tensor and is defined by

$$\boldsymbol{\epsilon} = \frac{1}{2} (\mathbf{H}_0^T \mathbf{G} \mathbf{H}_0^{-1} - \mathbf{1}) \quad 2.2$$

where $\mathbf{G} = \mathbf{H}^T \mathbf{H}$, superscript T represents matrix transposition and \mathbf{H}_0 is the reference value of matrix \mathbf{H} . The equations of motion obtained from Equation 2.1 are

$$m_a s^2 \frac{d^2 \rho_a}{dt^2} = F_a - m_a (s^2 \mathbf{G}^{-1} \frac{d\mathbf{G}}{dt} + 2s \frac{ds}{dt}) \frac{d\rho_a}{dt} \quad 2.3$$

$$W \frac{d^2 \mathbf{H}}{dt^2} = \mathbf{P} \mathbf{A} - \mathbf{H} \boldsymbol{\Gamma} \quad 2.4$$

$$Q \frac{d^2 s}{dt^2} = \frac{2K - (3N+1) k_B T_0}{s} \quad 2.5$$

where K is the kinetic energy and \mathbf{P} is the internal stress tensor, $\mathbf{A} = V \mathbf{H}^T$ is the area tensor and $\boldsymbol{\Gamma} = V \mathbf{H}^{-1} \mathbf{t} \mathbf{H}^T$ is a constant matrix.

In the thermodynamics of anisotropic solids, the enthalpy, H , of the system is

$$H = E + V_0 \text{Tr}(\mathbf{t} \boldsymbol{\epsilon}) \quad 2.6$$

where E is the internal energy, and the stress tensor is related to thermodynamic tension through

$$\boldsymbol{\sigma} = \frac{V_0}{V} \langle \mathbf{H} \rangle \mathbf{H}_0^{-1} \mathbf{t} \mathbf{H}_0^T \langle \mathbf{H}^T \rangle \quad 2.7$$

Here, $\langle \mathbf{H} \rangle$, is the equilibrium shape and size matrix for the system in this distorted state.

The following expressions for elastic coefficients, C_{ijkl} , and compliance tensor, S_{ijkl} , can be used to calculate them in molecular dynamics simulations

$$S_{ijkl} = - \frac{V_0}{k_B T} \langle \delta \epsilon_{ij} \delta \epsilon_{kl} \rangle \quad 2.8$$

$$C_{ijkl} = \frac{2Nk_B T}{V_0} (\delta_{ik} \delta_{lj} + \delta_{il} \delta_{kj}) - \frac{V_0}{k_B T} \langle \delta P_{ij} \delta P_{kl} \rangle + \langle \Xi_{ijkl} \rangle \quad 2.9$$

In these expressions, $\delta \mathbf{A} = \mathbf{A} - \langle \mathbf{A} \rangle$, and angular brackets represent averaging, δ_{ik} is the usual Kronecker tensor and finally Ξ_{ijkl} is the hyper virial tensor calculated from second derivatives of the potential. Even though the expression for compliance tensor Eq. (2.8) is simpler and can be calculated from a constant stress MD run, the convergence of strain fluctuations are found to be notoriously slow [3]. In our calculations we used the Eq. (2.9) which were previously shown to

be very efficient and feasible in calculating the elastic constants of van der Waals solids, metals, semiconductors.

There are similar expressions for other thermodynamic properties. We give the three isotropic response functions, compressibility, specific heat and thermal expansion constant which can all be calculated from constant temperature constant stress (TtN) molecular dynamics.

$$\kappa = - \frac{\langle \delta V \delta V \rangle}{\langle V \rangle k_B T} \quad 2.10$$

$$C_P = \frac{\langle \delta H \delta H \rangle}{k_B T^2} \quad 2.11$$

$$\alpha_P = \frac{\langle \delta H \delta V \rangle}{k_B T^2} \quad 2.12$$

where H is the enthalpy of the system, defined by Eq. 2.6.

FORCE FIELD PARAMETERS FOR POLYETHYLENE

We devote this section to describe the force field parameters used in modeling crystalline polyethylene. The interaction potential energy consists of valence and non bonded terms:

$$E = E_{val} + E_{nb}. \quad 3.1$$

where the valence and non bond interaction terms are given by the sum of various terms

$$E_{val} = E_b + E_a + E_t + E_x \quad 3.2$$

$$E_{nb} = E_{vdW} + E_{es} \quad 3.3$$

Here E_b is bond stretch, E_a is angle bend, E_t is torsional and E_x is the covalent cross terms while the non bond terms consist of only van der Waals and electrostatic interactions.

Pure valence interactions, bond stretch, angle bend and torsions are described by a Morse potential, harmonic cosine expression and a three fold cosine expansion, respectively.

$$E_b = D_b (e^{-\alpha(R-R_b)} - 1)^2 \quad 3.4$$

$$E_a = \frac{1}{2} C (\cos \theta - \cos \theta_a)^2 \quad 3.5$$

$$E_t = \frac{1}{2} V_1 (1 + \cos 3\phi) \quad 3.6$$

In the above expressions R is the length of the bond ij , R_b and D_b are the position and the depth of minima, θ is the angle between bonds ij and jk and θ_a is the equilibrium value of the angle; ϕ is the torsional angle between bonds ij , jk and kl and V_1 is the torsional barrier.

The bond-angle and bond-bond cross term is given as

$$E_{ax} = D_1 (\cos \theta - \cos \theta_a)(R_1 - R_{1b}) + D_2 (\cos \theta - \cos \theta_a)(R_2 - R_{2b}) + K_{rr} (R_1 - R_{1b})(R_2 - R_{2b}) \quad 3.7$$

where R_1 and R_2 are the bond lengths of bonds ij and jk ; $k_{r\theta} = -D \sin \theta$ is the angle-stretch force constant, k_{rr} is the stretch-stretch force constant. One center angle-angle term is

$$E_{1aa} = G (\cos \theta_{ijk} - \cos \theta_{aijk}) (\cos \theta_{ijl} - \cos \theta_{aijl}). \quad 3.8$$

Here, $K_{1\theta\theta} = G \sin \theta_{aijk} \sin \theta_{aijl}$ is the force constant for the two angle terms sharing the common bond ij . The two center angle-angle term is given by

$$E_{2aa} = F \cos \phi (\cos \theta_{aijk} - \cos \theta_{ajkl}) (\cos \theta_{ajkl} - \cos \theta_{ajkl}) \quad 3.9$$

where $K_{2\theta\theta} = F \cos \phi \sin \theta_{aijk} \sin \theta_{ajkl}$ is the force constant for two angles in which the central atoms j and k are bonded to each other.

The van der Waals interactions are represented by an exponential function,

$$E_{nb} = Ae^{-BR_{ij}} - \frac{C}{R_{ij}^6} = \frac{D}{(\zeta-6)} (6e^{-\zeta(1-\rho)} - \zeta\rho^6) \quad 3.10$$

where $\rho = R_{ij} / R_0$. The depth of the minima are $D_C=0.08444$ and $D_H=0.0160$ kcal/mol with minima occurring at $R_{0C}=3.8837$ and $R_{0H}=3.1975$ Å. The following scale factors are used for $\zeta_C=12.0$ and $\zeta_H=11.8$. C-H interaction parameters are obtained from the geometric mean of the given homonuclear parameters.

The electrostatic part of non bond interactions is described by the Coulomb expression

$$E_{es} = \frac{Q_i Q_j}{\epsilon_0 \epsilon R_{ij}} \quad 3.11$$

Q_i is the charge on atom i , in units of electronic charge, $1/\epsilon_0 = 332.0637$ gives the energy results in kcal/mole when the distance is in Å. The partial charge on Hydrogen was chosen as 0.144 lel and the charge on the Carbon was chosen as -0.288 lel based on earlier quantum mechanical calculations [5].

Table 1 shows the values of the valence interaction parameters used in our calculations. All the valence interaction parameters were obtained by using the Hessian Biased Optimization method [6] and the details were described elsewhere [7].

Table 1. Valence force field parameters for polyethylene. a) bond-stretch ; b) angle-bend; c) torsion; d) the one center angle-angle term (values of G); e) the two center angle-angle (values of F); and f) the angle cross term.

	R_b	k_b	D_b
C-C	1.4841	884.994	85.80
C-H	1.0765	741.372	95.10

a

	H-C-H	C-C-H	C-C-C
k_θ	55.6076	65.7301	84.1810
θ	119.3933	117.7291	121.2400

b

	H-C-C-H	C-C-C-H	C-C-C-C
V_t	5.1686	6.1626	5.7070

c

	CC:HC	CC:HH	CH:CC	CH:CH
	-7.6083	-5.3356	-5.0824	-5.3356

d

	H:CC:H	C:CC:H	C:CC:C
	-17.7274	-16.4004	-21.5910

e

	H-C-H	C-C-H	C-C-C
D_1	-22.6583	-34.3195	-54.0185
D_2	-22.6583	-25.9234	-54.0185
k_{12}	3.1321	1.3684	26.2187

f

MOLECULAR DYNAMICS CALCULATIONS

Most of the calculations are performed on a 360 atom system, $2 \times 3 \times 5$ unit cells. To check the size dependence runs with a single unit cell and $2 \times 3 \times 7$ unit cells are performed. The simulations are carried out at temperatures 77, 100, 200, and 300 K. System is maintained at constant temperature by applying Nose thermostat [2]. In order to obtain equilibrium reference state at each temperature zero-stress simulations performed using TtN molecular dynamics, *i.e.* Eqs 2.3-2.5 were solved. The masslike parameters W and Q are chosen as described in the references [8,9]. The integration time step used in solving these

equations were 1 fs and the lengths of simulations were 10 ps for 77 and 100K 15 ps for 200K and 20 ps for 300 K runs. After the equilibrium values of reference states, H_0 and V_0 , at each temperature were obtained the simulations for obtaining elastic constants were conducted at constant temperature and constant volume and shape, i.e. (THN) molecular dynamics. In these runs, we adopted a smaller time step for higher temperature simulations (at 200 and 300K 0.5 fs is used).

In figure 1, we display the variation and running average of lattice parameters for 200K simulation. Especially the fluctuation in c (the chain direction) is very small compared to a and b . A 15 ps run was enough to obtain the average values for the lattice parameters. The system retained its shape (the deviations in cell angles from orthogonality was largest at 300 K, less than 1° , at lower temperatures the deviations were less than 0.1°). The calculated lattice constants were 7.301, 4.856, 2.543 Å at 100 K; 7.647, 4.747, 2.543 Å at 200 K and 7.895, 4.755, 2.535 Å at 300 K. The calculated volumes per unit cell are 89.42 (88.60), 90.18 (88.92), 92.31 (91.00) and 95.17 (93.15) Å³, the numbers in parentheses are the experimental values obtained from Swan [10] and Avitable *et. al.* [11]. The deviation of calculated value of volume from the experimental value is less than 3% percent even at the highest temperature simulation (300K).

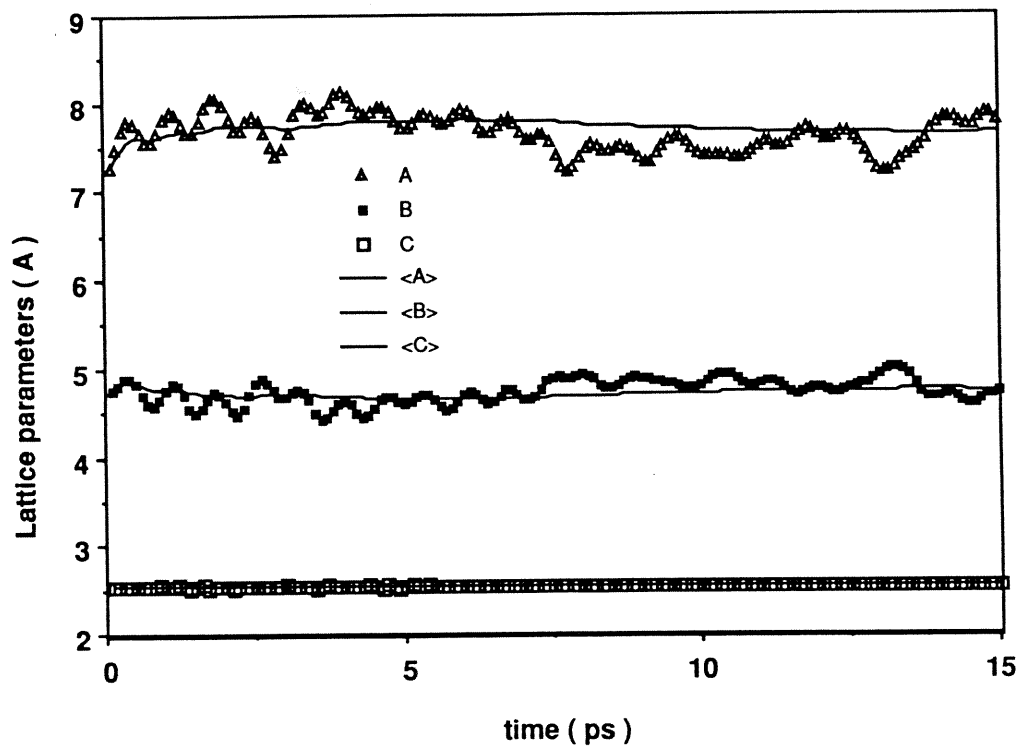


Figure 1. Variations and running averages of the lattice constants of polyethylene at 200 K obtained from isothermal zero stress simulation.

Due to the symmetry of the crystal, polyethylene has only 12 nonzero elastic constants, 9 of which are independent. The contributions to these elastic constants from hyper virial at the simulated temperatures are listed in Table 2, the last term in Eq. 2.9. The long range non bond and electrostatic contributions to the hyper virial tensor and stresses are also taken into account by using the Accuracy Bounded Convergence Acceleration (ABCA) implementation [12] of the Ewald summation technique.

Table 2. Calculated contribution to elastic constants of crystalline polyethylene from the hyper virial term. Voigt notation is used and the values are in GPa.virial term.

T	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₂₃
77	13.5	11.4	336.4	4.09	2.39	6.15	6.88	1.82	3.64
100	11.2	11.1	332.7	4.27	2.26	4.78	6.20	1.41	3.51
200	5.1	7.2	325.0	4.24	2.67	4.10	7.84	1.39	3.12
300	3.1	4.2	315.3	2.57	1.84	3.38	6.55	1.22	1.94

The observed trend in the elastic coefficients is an obvious softening as the temperature increases, as it is expected. Similar trend is observed in earlier molecular mechanics calculations of elastic coefficients using the experimental lattice parameters [7]. The thermal contributions, the first term in Eq. 2.9, for C₁₂, C₁₃, and C₂₃ are zero and contribution for C₁₁, C₂₂, C₃₃ are 2.28, 2.94, 5.74, 8.36 GPa and the contribution for C₄₄, C₅₅, C₆₆ are 1.14, 1.47, 2.87, 4.18 GPa, at 77, 100, 200, 300K respectively. The thermal and hyper virial contributions to elastic constants converge faster compared to the contribution from stress tensor fluctuations. Simulations Twenty to fifty picosecond simulations have not yielded reasonable convergence in the stress-stress fluctuations. Same length simulations yield converged stress fluctuations to accurately estimate the elastic constants in van der Waals solids [3], metals [4], simulations less than 100 ps long gave accurate estimations even for the third order elastic constants [13]. The current length of simulations, 20 ps to 50 ps, show that for polymeric systems containing high frequency modes of motion due to covalent interaction force constants require longer simulation times in order to accurately estimate the contributions from stress fluctuations. To check the convergence, we used the fluctuation terms which needs to be zero by symmetry, for instance C₁₄, is on the order of a few GPa. Since the hyper virial and thermal contributions for some of the elastic constants are on the same order as these fluctuations, the simulations need to be extended to longer times especially for estimating the components other than the coefficient along the chain direction, C₃₃.

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