Thermochimica Acta, 214 (1993) 103–109
Elsevier Science Publishers B V., Amsterdam

MOLECULAR DYNAMICS SIMULATION AND THERMAL ANALYSIS OF MACROMOLECULAR CRYSTALS

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ABSTRACT

Macromolecular crystals are not in equilibrium and their structure is governed by crystal structure and macroconformation rules. Our *A*dvanced *TH*ermal *A*nalysis *S*ystem, *ATHAS*, has led in the last 15 years to the description of more than 150 polymers and polymer-related, small model compounds. The discussion of the entropy and the detailed study of heat capacities has resulted in better understanding of disorder and motion in many crystalline polymers. To get more insight, molecular dynamics simulations on supercomputers were used in cooperation with Drs. D. W. Noid and B. G. Sumpter of our institutions. At present, crystals with 9600 chain atoms can be simulated for times of up to 0.1 ns. The computed thermal effects agree with measurements, making the supercomputer a direct calorimetric simulator that links macroscopic observations with microscopic mechanics.

Introduction

The description of matter is commonly accomplished on two levels, the microscopic and the macroscopic level. The former permits a visualization of structure on an atomic or nanometer-size scale, while the latter fits the human senses, i.e. it involves a scale larger than one micrometer. The difference in macroscopic and microscopic length scale is thus at least a factor of 10^4. For a full description of matter one needs to discuss, however, also the molecular motion. In this case, the atomic time scale is in the picosecond range, while the shortest time scale of direct, macroscopic observation is, at best, in the millisecond range. To bridge the two time scales, one needs at least a factor of 10^9. Understanding molecular motion is, thus, much more difficult than visualizing the atomic structure.

The microscopic structure of linear macromolecules in the crystalline state is well described by knowledge derived mainly from X-ray and electron diffraction experiments.[1] The macroscopic structure is known from optical microscopy.[1,2] In this presentation, I would like to concentrate on the description of molecular motion, the

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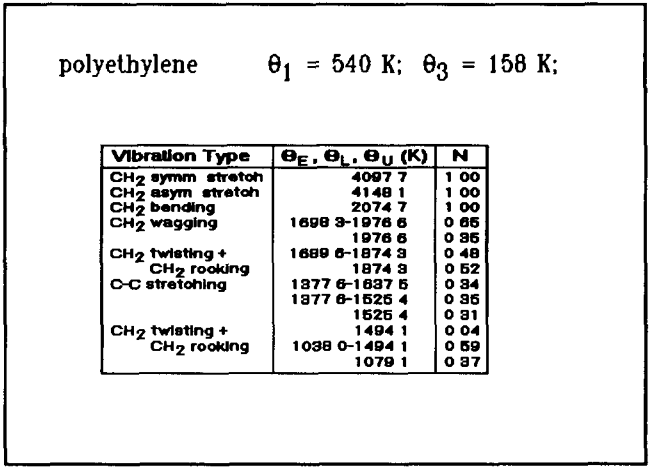
This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992 topic closely linked with thermal analysis. The macroscopic effects of this motion are prominently assessed by calorimetry. For many years calorimetry, as branch of thermal analysis, was the central theme of our *A*dvanced *TH*ermal *A*nalysi*S* laboratory, *ATHAS*.[3] The microscopic description of motion became possible only more recently through molecular dynamics simulations on supercomputers. It was possible to accomplish sufficiently long simulations of large enough crystal segments to link microscopic motion with macroscopic effects. The simulation is based on uniquely efficient computer codes developed by Dr. D. W. Noid.[4] All simulations were carried out as a cooperative effort with Drs. D. W. Noid, B. G. Sumpter, and Mr. G. Liang.

The THermal Analysis System, ATHAS

The *ATHAS* starts with extrapolation of data measured on metastable crystals to equilibrium [5,6] and conversion of constant pressure data to constant volume.[7] A detailed accounting of the experimental methods can be found in Refs. [3], [8] and [9]. Typically, heat capacities of semicrystalline macromolecules change with crystallinity at low temperature (<50 K) and within about 150 K of melting. Data on almost 150 different linear macromolecules have been collected in the 1990 version of the *ATHAS* Data Bank.[10] The first extrapolated data of this nature were derived in 1962.[11]



polyethylene $\theta_1 = 540$ K; $\theta_3 = 158$ K;

Vibration Type	$\Theta_E, \Theta_L, \Theta_U$ (K)	N
CH_2 symm stretch	4097 7	1 00
CH_2 asym stretch	4148 1	1 00
CH_2 bending	2074 7	1 00
CH_2 wagging	1698 3-1976 6	0 65
	1976 6	0 35
CH_2 twisting + CH_2 rocking	1689 6-1874 3	0 48
	1874 3	0 52
C-C stretching	1377 6-1637 5	0 34
	1377 6-1525 4	0 35
	1525 4	0 31
CH_2 twisting + CH_2 rocking	1494 1	0 04
	1038 0-1494 1	0 59
	1079 1	0 37

Figure 1. The approximate frequency spectrum.

With the heat capacities of many crystals known, one can make an attempt at understanding of the microscopic cause of the heat capacity. The major link of heat capacity is naturally to the vibrations in the crystal.[6] The overall vibrational spectrum is somewhat arbitrarily divided into group and skeletal vibrations. For polyethylene it is easy to identify seven group vibrations. Their frequency ranges, number of vibrations, *N*, and approximate description is given in Fig. 1. A detailed discussion of the frequency spectrum of crystalline polyethylene, as derived from normal mode calculations, is given in Ref. [12]. An Einstein function is used for the calculation of the heat capacity contribution from relatively sharp group vibrations (CH_2 stretching and bending vibrations). The broader distributions are broken into box distributions. Their heat capacity contributions are computed with one-dimensional Debye functions making use of the lower and upper vibration frequencies of the distributions. The skeletal vibrations reach into the acoustic range and are only poorly represented by normal mode calculations.[13] It became thus necessary to use the experimental heat capacities to derive an approximate vibrational spectrum. The Tarasov function satisfies the need for an approximate skeletal vibration spectrum. It can be fitted to the appropriate skeletal heat capacity with two frequency parameters Θ_1 and Θ_2 and consists of a three-dimensional Debye function segment for the intermolecular vibrations ($0 \leq \nu \leq \nu_3$) and a box distribution for the intramolecular vibrations ($\nu_3 \geq \nu \geq \nu_1$). For the purpose of calorimetric calculations, frequencies, ν, are expressed in this discussion in units of kelvin (temperature), Θ (1 Hz = 4.8×10^{-11} K, frequency expressed as $h\nu/k$).

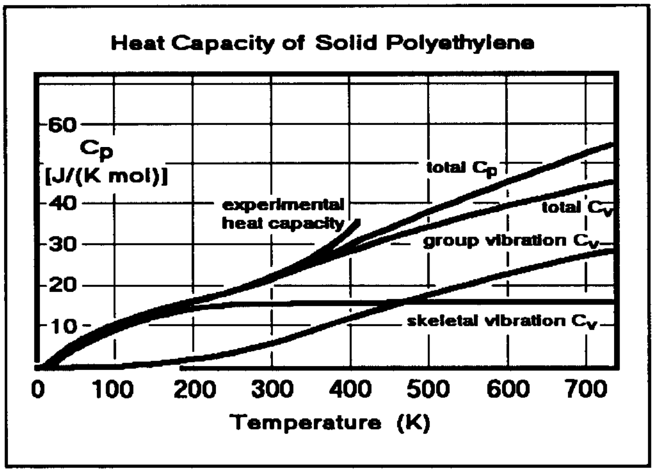


Figure 2. ATHAS computation and experimental data.

Finding now the best fit between experimental heat capacity and computed heat capacity based on the approximate frequency spectrum of Fig. 1 leads to the results shown in Fig. 2. Many of the features of the experimental heat capacity are fully duplicated. One major deviation, however, needs further discussion. Between 350 K and the equilibrium melting temperature (414.6 K) the experimental heat capacity is increasingly larger, reaching ultimately an excess of 23%, with a typical experimental precision in C_p of 1–5%. Besides polyethylene, more than one hundred other polymers have been analyzed and experience has been gained in the correlation of structure and the prediction of the thermodynamic functions. The change of heat capacity with structure of some paraffins with even numbers of carbon atoms can be seen in Fig. 3.[14] All show similar increases of the measured heat capacity before melting as was seen in the polyethylene of Fig.2.

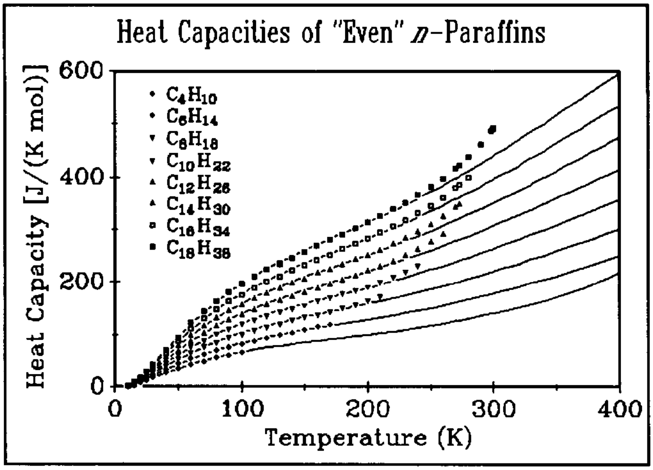


Figure 3. Experimental and computed heat capacities.

While computations of heat capacities of solids from approximate vibrational spectra is feasible, the link of heat capacities of liquid polymers to the microscopic motion is more difficult.[15] It was found empirically that many heat capacities of liquids are additive with respect to their structural components. An example of such additivity is shown in Fig. 4.[16] The equation in the figure is represented by the thin lines. The thick lines indicate the experimental data.

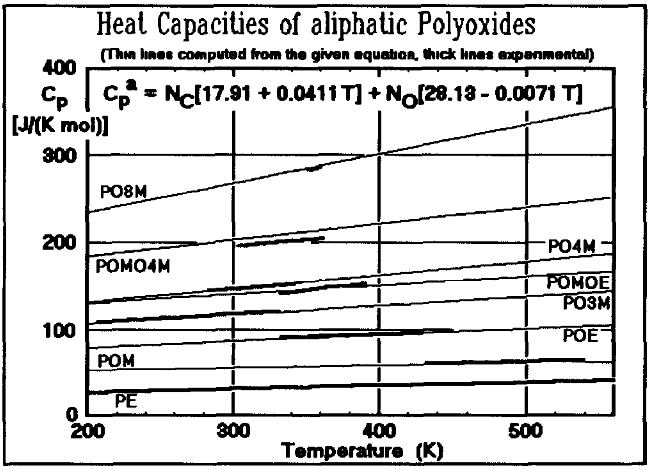


Figure 4. Heat capacities of the liquid state.

With both, liquid and solid heat capacities known, it is now possible to derive the full thermodynamic functions and discuss the stability of the phases through the Gibbs function, *G*; the order, through the entropy, *S*; and the energetics, through the enthalpy, *H*. Figure 5 shows a typical example. Two-stage fusion as seen in the *trans*-1,4-polybutadiene has led to the identification of conformational disorder as a special mesophase in macromolecules.[17,18] The needed transition parameters (the heats of transition and equilibrium transition temperatures) have been reviewed and discussed in detail in an earlier treatise.[5]

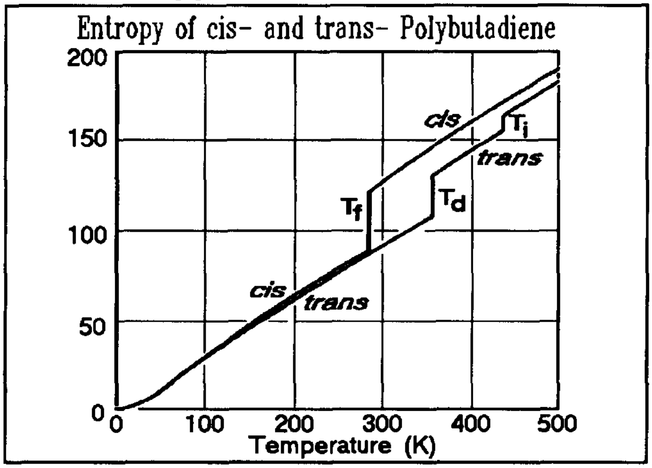


Figure 5. Entropy of the polybutadienes.

Against the background of equilibrium behavior, it became also increasingly possible to analyze nonequilibrium behavior. One of the long-expected observations is that of a rigid amorphous solid in semicrystalline polymers. This metastable solid above the glass transition temperature, T_g, of the unaffected material can be detected by the smaller increase in heat capacity, ΔC_p, at T_g than expected from the crystallinity evaluated from the heat of fusion.[19] Rigid amorphous fractions are particularly prevalent in macromolecules that contain rigid segments, such as phenylene groups.[20] A rigid amorphous fraction is expected to increase the modulus and should decrease on annealing at a temperature that permits relaxation of the strain exerted by the crystals on the amorphous phase. Particularly affected should be drawn fibers.

The Simulation of Motion in Polymer Crystals

To realistically simulate vibrational as well as large-angle motion in a macromolecular crystal, a chain of 25 – 100 atoms of mass 14 each (collapsed CH_2-groups) was set on lattice position of a polyethylene crystal and surrounded by various shells of mobile chains. The simulation involves then the setting-up of a proper Hamiltonian for the system. The potential energy is accounted for by a Morse potential for the bond-interaction of neighboring atoms along the mobile chain, a quadratic bending potential for successive three-atom motion, and a torsional potential to simulate the four-atom, internal rotations. Finally, a Lennard-Jones 6,12 potential is set up for the nonbonded interactions between all atoms. The detailed programming strategy and potential functions are given in Refs. [4]. Hamilton's equations are then integrated in cartesian coordinates using a vectorized version of a differential equation solver after a randomly chosen amounts of kinetic energy are placed on the dynamic chains to produce the desired temperature. The computations were carried out on a Cray XMP or an IBM 3090 computer. The first results were published in 1989.[21] Typical simulations run between 10 and 100 ps and use up to 16 h supercomputer time. Figure 6 shows a result for 430 K. In this simulation seven mobile chains, contained by twelve rigid chains, were used. Depicted are the lower 40 chain atoms of the mobile chains of the crystal. Immediately after the beginning of the simulation a considerable number of large torsional displacements can be observed. This is a behavior one would expect of a conformationally disordered crystal. Under the chosen simulation conditions, the first large-angle displacements occur at 320 K. Computing heat capacity from the difference in energy needed for simulations at different temperatures, one finds that this appearance of defects is linked with the positive heat capacity deviation observed experimentally (see Fig. 3).[21] A detailed discussion of the vibrational

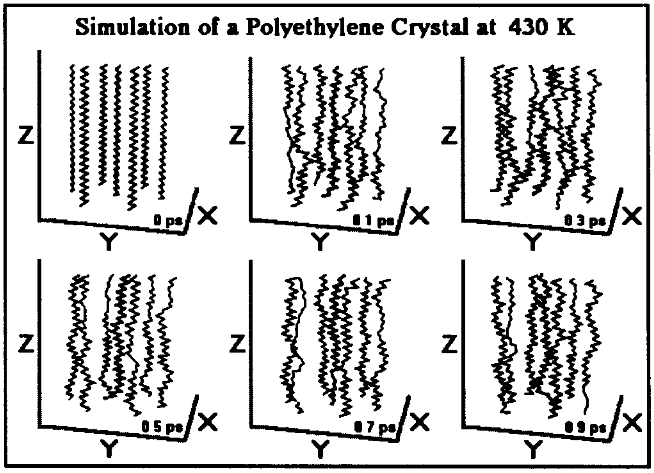


Figure 6. Simulation of a polymer of seven chains.

spectrum of the simulation is given in Ref. [22]. Typical rates of attainment of torsional deviations of more than 90° are from 10^{10} to 10^{11} s^{-1} at 350 K for any atom in the center chain. These defects cause a continuous decrease in the end-to-end distance as the temperature increases.[23]

Another question that can be addressed with the results of the simulations is the behavior and lifetime of the conformational defects.[23,24] These defects play a central role in the annealing and deformation processes, known to occur in crystals of linear macromolecules.[1] Figure 6 illustrates the lifetimes of defects in a polyethylene-like crystal at the high temperature of 440 K. The high temperature was chosen to increase the number of defects in the limited time available for such simulations. It can be clearly seen that the defects are randomly generated and have lifetimes in the picosecond range. The lifetimes increase as soon as sequences of *gauche* and *trans* defects are created. These defects keep the chains largely parallel. One must suggest that at the temperatures where annealing or deformation of metastable crystals is possible, the randomly generated defects initiate the macroscopically observed changes.[24] It could be shown that threshold energies exist, for example, for the pulling of a chain out of a crystal. These energies are, as expected, temperature and chain-length dependent.[25] Even the melting process can be simulated, giving initial information on the mechanism.[26]

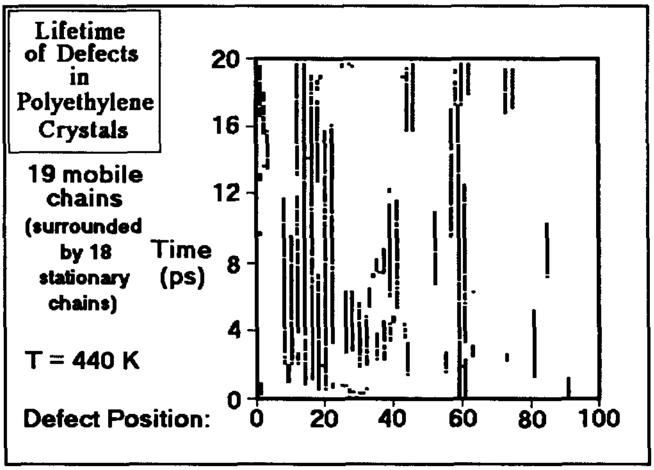


Figure 7. Lifetime of gauche defects.

The combination of measurements of thermal properties, use of approximate interpretations of vibrational spectra, empirical addition schemes, and molecular dynamics simulations are on the threshold to significantly advance the understanding of polymer crystals.

ACKNOWLEDGEMENTS

This work was supported over the years mainly by the Division of Materials Research, National Science Foundation, Polymers Program, present Grant # DMR 88-18412, and since 1988 also by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

[1] B. Wunderlich, "Macromolecule Physics, Vols. 1 and 2", Academic Press, New York, NY, 1973, 1976.

[2] L. Sawyer and D. T. Grubb, '"Polymer Microscopy." Chapman and Hall, New York, NY; A. E. Woodward, "Atlas of Polymer Morphology." Hanser Publ. New York, NY, 1988.

[3] B. Wunderlich, "Thermal Analysis." Academic Press, New York, NY, 1990.

[4] D. W. Noid, B. G. Sumpter, B. Wunderlich, and G. A. Pfeffer, *Comp. Chem.* **11**, 263 (1990); D. W. Noid, B. G. Sumpter and B. Wunderlich, *Macromolecules*, **23**, 664 (1990).

[5] B. Wunderlich, "Macromolecular Physics, Vol. 3," Academic Press, New York, NY, 1980.

[6] B. Wunderlich and H. Baur, *Adv. Polymer Sci.*, **7**, 151 (1970).

[7] R. Pan, M. Varma-Nair, and B. Wunderlich, *J. Thermal Anal.*, **35**, 955 (1989).

[8] B. Wunderlich and S. Z. D. Cheng, *Gazz. Chim. Italiana*, **116**, 345 (1986).

[9] B. Wunderlich, *Shin Netsu Sokuteino Shinpo*, **1**, 71 (1990).

[10] M. Varma-Nair and B. Wunderlich, *J. Phys. Chem. Ref. Data*, **20**, 349 (1990); and nine earlier publications in the same journal.

[11] B. Wunderlich, *J. Chem. Phys.*, **37**, 1203, 1207, 2429 (1962); see also *J. Polymer Sci., Part C*, **1**, 41 (1963).

[12] J. Barnes and B. Fanconi, *J. Phys. Chem. Ref. Data*, **7**, 309 (1978).

[13] H.-S. Bu, *J. Phys. Chem.*, **91**, 4179 (1987).

[14] Y. Jin and B. Wunderlich, *J. Phys. Chem.*, **95**, 9000 (1991).

[15] K. Loufakis and B. Wunderlich, *J. Phys. Chem.* **92**, 4205 (1988).

[16] H. Suzuki and B. Wunderlich, *J. Polymer Sci., Polymer Phys. Ed.*, **23**, 1671 (1985).

[17] B. Wunderlich and J. Grebowicz, *Adv. Polymer Sci.*, **60/69**, 1 (1984).

[18] B. Wunderlich, M. Möller, J. Grebowicz and H. Baur, "Conformational Motion and Disorder in Low and High Molecular Mass Crystals." Springer Verlag, Berlin, 1988 (*Adv. Polymer Sci.*, Volume **87**).

[19] H. Suzuki, J. Grebowicz, and B. Wunderlich, *British Polymer Journal*, **17**, 1 (1981).

[20] S. Z. D. Cheng, M.-Y. Cao, and B. Wunderlich, *Macromolecules*, **19**, 1868 (1986); S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, *Macromolecules*, **20**, 2801 (1987)

[21] D. W. Noid, B. G. Sumpter, M. Varma-Nair and B. Wunderlich, *Makromol. Chemie, Rapid Commun.*, **10**, 377 (1989).

[22] D. W. Noid, B. G. Sumpter and B. Wunderlich, *Analytica Chemica Acta*, **235**, 143 (1990).

[23] B. G. Sumpter, D. W. Noid, and B. Wunderlich, *J. Chem. Phys.*, **93**, 6875 (1990).

[24] B. G. Sumpter, D. W. Noid, and B. Wunderlich, *Macromolecules*, to be published (1992).

[25] D. W. Noid, B. G. Sumpter and B. Wunderlich, *Polymer Communications*, **31**, 304 (1990).

[26] B. G. Sumpter, D. W. Noid, B. Wunderlich and S. Z. D. Cheng, *Macromolecules*, **23**, 4771 (1990).