*Thermochimica Acta*, 119 (1987) 225-230
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

# THE COMPUTATION OF HEAT CAPACITIES OF SOLID HIGH POLYMERS FROM VIBRATIONAL SPECTRA

B. WUNDERLICH[1] and H.S. BU[2]

[1]Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, 12180-3590 (USA). Present Address: Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 (USA)

[2]Department of Chemistry, Fudan University, Shanghai, China.

## SUMMARY

Based on experimental data collected over the last 15 years (ATHAS data bank) a system has been developed that permits the computation of the heat capacities of solid polymeric materials. It relies on separation of the vibrational spectrum into group and skeletal vibrations. The former are known from computations fitted to IR and Raman data, the latter can be fitted to low temperature heat capacities using the Tarasov equation. Knowing the chemical structure, the parameters of the Tarasov equation may be predicted by comparison with known heat capacities of related materials. Agreement between prediction, computation and experiment is usually better than ± 5 %.

## INTRODUCTION

The computation method of heat capacities to be discussed here is part of our Advanced Thermal Analysis System (ATHAS, ref. 1) which is based not only on work of our laboratory, but uses also the collective work of all other laboratories. First, a critically reviewed data bank was established (ref. 2). Work on instrumentation improvement (ref. 3), development of computation programms (ref. 4) and the theory of heat capacities (ref. 5) completed the background for the broad-ranging discussion of heat capacities of solids to be summarized here. The detailed publications can be found in refs. 6 and empirical addition schemes for heat capacities were derived (ref. 7).

## HEAT CAPACITY DESCRIPTION

The head capacity of linear macromolecules is best subdivided into four temperature regions. Heat capacities below 5 - 10 K, though interesting from a theoretical point of view, will not be treated here in detail since they contribute only little to the integral thermal properties at higher temperature. They are strongly dependent on the physical state (crystalline,amorphous, or semicrystalline).

In the 10 to 100 K temperature range, heat capacity measurements are completely dominated by adiabatic calorimetry. The theory of heat capacity is well understood. Since practically all macromolecules are solids below 100 K, i. e. glassy, crystalline, or partially crystalline and partially glassy, the heat capacity is of vibrational origin and well described by the harmonic oscillator approximation. It proved useful to separate the vibrations into skeletal and group vibrations. The former are of relatively low frequency, strongly coupled, and represent the intra- and inter-molecular vibrations of the chain molecules as a whole. They can be modelled by making the assumption that the atoms are attached rigidly to the backbone chain. The skeletal vibrations dominate the heat capacity in this 10 to 100 K temperature range. All effort to calculate the intermolecular, skeletal vibrations from crystal-structure and force-constant data alone have badly failed in the past. Heat capacity measurements provide the best means for evaluation of the low-frequency, integral vibrational spectrum. The intramolecular skeletal vibrations are somewhat higher in frequency and are accessible in their upper frequency range through isolated-chain,normal mode calculations. Such calculations also permit the evaluation of the usually numerous group vibrations. Once the vibrational spectrum is established, the heat capacity (at constant volume) can be calculated up to high temperatures.

The Einstein function (ref. 8) inverts frequency of the spectrum to its heat capacity contribution and vice versa, so that the overall heat capacity is:

$$C_V/(NR) = \int_0^{\Theta_{max}} \frac{(\Theta/T)^2 \exp(\Theta/T)}{[\exp(\Theta/T)-1]^2} d\Theta \qquad 1$$

where T is the temperature and $\Theta$ is the frequency, both expressed in kelvin ($\Theta = h\nu/k$ with $\nu$ representing the frequency in Hz, h and k are Planck's and Boltzmann's constant, respectively; 1 Hz is $4.799 \times 10^{-11}$ K, 1 $cm^{-1}$ = 1,4388 K). The integral extends over all skeletal and group vibrations.

The integral of eq. 1 is evaluated in steps. The lowest vibrational frequencies (skeletal) usually follow a quadratic function up to a frequency limit called $\Theta_D$ or $\Theta_3$. This is the well-known Debye approximation (ref. 9) of low temperature heat capacities.

$$D_3\left(\frac{\Theta_D}{T}\right) = \frac{C_v}{NR} = (12T^3/\Theta_3^3)\int_0^{\Theta_3/T} \frac{x^3 dx}{\exp(x)-1} - \frac{3\Theta_D/T}{\exp(\Theta_D/T)-1} \qquad 2$$

For two- or one-dimensional structures such as found in crystals of layer and chain molecules the frequency distribution changes to a linear and constant function, respectively. These intergrals are called the two-(ref. 10) and one-dimensional (ref. 11) Debye functions.

$$D_2\left(\frac{\Theta_2}{T}\right) = \frac{C_v}{NR} = (6T^2/\Theta_2^2)\int_0^{\Theta_2/T} \frac{x^2 dx}{\exp(x)-1} - \frac{2\Theta_D/T}{\exp(\Theta_2/T)-1} \qquad 3$$

$$D_1\left(\frac{\Theta_1}{T}\right) = \frac{C_v}{NR} = (2T/\Theta_1)\int_0^{\Theta_1/T} \frac{x\, dx}{\exp(x)-1} - \frac{\Theta_1/T}{\exp(\Theta_1/T)-1} \qquad 4$$

N in eqs. 1 - 4 refers to the appropriate number of vibrators and $x = h\nu/kT = \Theta/T$. The sum of all N is three times the number of atoms in a repeating unit, the number of degrees of freedom. Tarasov (ref. 12) proposed a combination of eqs. 2 and 4 for the skeletal vibrations of a linear chain

$$T(\Theta_3/T, \Theta_1/T) = C_V/NR = D_1(\Theta_1/T) - \Theta_3/\Theta_1[D_1(\Theta_3/T) - D_3(\Theta_3/T)] \qquad 5$$

This equation was shown on the examples to hold for most linear macromolecules to a precision of several per cent. Its limits are reached when phenylene groups are included in the backbone chain as in poly(phenylene oxide) or poly(ethylene terephthalate), or alternating heavy and light mass backbone unit occur, as in poly(vinylidene fluoride) or poly(vinilidene chloride).

For the group vibrations which are of much narrower distribution it is usually sufficient to use single frequency Einstein terms or to average over a frequency range which leads to a box distribution function.

$$B(\Theta_U/T, \Theta_L/T) = C_V/NR = \Theta_U/(\Theta_U-\Theta_L)[D_1(\Theta_U/T) - (\Theta_L/\Theta_U)D_1(\Theta_L/T)] \qquad 6$$

where $\Theta_U$ and $\Theta_L$ are the upper and lower frequencies of the group-vibration range.

The final step of computation is to connect $C_v$ with the measured $C_p$. For this purpose one can use the thermal expansivity $\alpha$ and the isothermal compressibility $\varkappa$.

$$C_p\text{-}C_V = \alpha^2 VT/\varkappa \qquad 7$$

Since $\alpha$ and $\varkappa$ are usually, at best, available at one temperature, one makes often use the semiempirical Lindemann expression:

$$C_p\text{-}C_V = C_p{}^2(T/T^\circ{}_m)A_o \qquad 8$$

where $T^o{}_m$ is the equilibrium melting temperature and $A_o$ is a constant which for many polymers has a value close to $5.11 \times 10^{-3}$ Kmol/J (per mole of heavy atoms).

The next temperature region is from about 100 K to the glass or melting transition. Solid heat capacities are practically independent of crystallinity in this temperature range. Most measurements are made by differential scanning calorimetry (DSC). In most cases it is possible, after computation of the group vibrations, to evaluate the intramolecular skeletal vibrations. The intermolecular vibrations are commonly already excited at these temperatures and thus contribute a constant amount to the heat capacity. Of special problem are the semicrystalline macromolecules between the glass and melting transitions. They have a microphase-separated, twophase structure with most molecules bridging both phases. This special influence of phase boundaries on molecular mobility gives rise to positive and negative $C_p$-deviations from the value computed under the assumption of a macroscopic, two-phase system (crystallinity model). The deviations from the purely vibration and liquid $C_p$ permit to analyze such structure-sensitive properties.

The last temperature range is that of the liquid state, it starts at the glass transition or at the melting temperature. Very little theoretical knowledge exists about its heat capacity, except that the group vibrations change little on fusion. The change of the skeletal vibrations in frequency due to the volume expansion is also of little influence on heat capacity, since, once excited, the heat capacity contribution of a vibrational degree of freedom remains unchanged on lowering of the frequency. The change in volume-expansion makes itself felt through a sizeable increase in $C_p$ at the glass transition, caused largely by potential energy increase (hole formation). Empirically liquid heat capacities are often changing linearly with temperature.

## CONCLUSIONS

Starting from a detailed analysis of heat capacity of linear macromolecules, it has been shown that considerable advance in thermal analysis is possible. Not only can the equilibrium thermodynamic properties be better established and linked to fundamental, atomic-scale properties, such as the vibrational frequency spectrum and order as well as mobility, but it is also possible to discuss non-equilibrium states crystalline, and microphase-separated polymers.

## ACKNOWLEDGEMENTS

This work was supparted by the polymers program of the Natl. Sci. Foundation of the US (Grant No. DMR 83-17097). Write-up and presentation of this paper was made possible by a Senior US Scientist Award of the Alexander von Humboldt Stiftung (B.W., 1987/88).

## REFERENCES

An entrance to the large literature in thermal analysis is offered through the following ATHAS publications.

1 Description and projections of ATHAS: U. Gaur, B. Wunderlich, Am. Chem. Soc. Symp. Ser., 197, T. Provder, Ed., The American Chemical Society, Washington, D. C., 1982, B. Wunderlich, Am. Lab., 14,28 (1982). For biannual ATHAS reports write to the author.

2 The ATHAS data bank 1980: J. Gaur, S.-F. Lau, H.-C. Shu, B.B. Wunderlich, A. Mehta, B. Wunderlich, J. Phys. Chem. Ref. Data, 10,89 (1981); ibid.,10, 119 (1981); ibid., 10, 1001 (1981); ibid., 10, 1051 (1981); ibid., 11, 313 (1982); ibid., 11, 1065 (1982); ibid., 12, 29 (1983); ibid., 12, 65 (1983); ibid., 12, 91 (1983); for reprints,order from the American Chemical Society, 1155 Sixteenth St. NW, Washington, D. C., 20036 (USA).

3 Instrumentation:
H. Suzuki, B. Wunderlich, J. Thermal Anal., 29, 1369 (1985); B. Wunderlich, R. C. Bopp, ibid., 6, 355 (1974); A. Mehta, R. C. Bopp, U. Gaur, B. Wunderlich, ibid., 13, 71 (1978); ibid., 13, 197 (1978). See also: B. Wunderlich, DTA, in A. Weissberger and B. W. Rossiter, Eds., Physical methods of chemistry, J. Wiley & Sons, New York, 1971, Vol. 1, Part V, Chapter 8, p. 427.

4 Computations:
Yu. V. Cheban, S.-F. Lau, B. Wunderlich, Colloid Polymer Sci., 260, 9 (1982); S.-F. Lau, B. Wunderlich, J. Thermal Anal., 28, 59 (1983); J. Grebowicz, B. Wunderlich, ibid., 30, 227 (1985).

5 Theory of heat capacity. H. Baur, B. Wunderlich, Advan. Polymer Sci., 7, 151 (1970); Russian translation, MIR, Moscow, 1972; see also: B. Wunderlich in Thermal characterization of polymeric materials, E. Turi, Ed., Academic Press New York, 1981; H. S. Bu, S. Z. D. Cheng, B. Wunderlich, J. Phys. Chem. to be published 1987.

6 Polymer analyses; a) selenium: P. H. - C. Shu, B. Wunderlich in Thermal analysis in polymer characterization, E. Turi, Ed., J. Wiley & Sons, Ltd., London, 1981, p. 124; b) polyethylene and polyoxides: J. Grebowicz, H. Suzuki, B. Wunderlich, Polymer, 26, 561 (1985); J. Polymer Sci., Polymer Phys. Ed., 23, 1671 (1985); Macromol. Chem., 186, 1109 (1985); c) fluoro and chloro polymers: K. Loufakis, B. Wunderlich, Polymer, 26, 1875 (1985); d) polypropylene: J. Grebowicz, S.-F. Lau, B. Wunderlich, J. Polymer Sci., Polymer Symposium, 71, 19 (1984); e) branched polyethylenes: W. Aycock, B. Wunderlich, Polymer, submitted for publication; g) polyesters: S. Lim, B. Wunderlich, Polymer, 28, 777 (1987); h) polysterene, substituted polystyrenes and polyparaxylylene: D. Kirkpatrick, L. Judovits, B. Wunderlich, J. Polymer Sci., Polym. Phys. Ed., 24, 45 (1986); and ibid. 24, 2725 (1986); i) polyacrylates and methacrylates: H.-S. Bu, B. Wunderlich, Polymer, to be published; phenylene containing polymers: S. Z. D. Cheng, B. Wunderlich, J. Polymer Sci., Polymer Phys. Ed. 24, 1755 (1986); S. Z. D. Cheng, S. Lim, L. H. Judovits, B. Wunderlich, Polymer, to be publishes 1987.

7 Addition scheme for heat capacities: B. Wunderlich, L.D. Jones J. Macromol. Sci., B3, 67 (1969); U. Gaur, B. Wunderlich, Polymer Div., Am. Chem. Soc., Preprints, 20, 429 (1979); B. Wunderlich, U. Gaur, Thermal analysis, W. Hemminger, Ed., Birkhauser, Basel, 1980, Vol. 2, p. 409; U. Gaur, M.-Y. Cao, R.Pan, B. Wunderlich, J. Thermal Anal., 31, 421 (1986); R. Pan, M.-Y. Cao, B. Wunderlich, ibid., 31, 1319 (1986).

8 Einstein function table: Natl. Bureau of Standards, Monograph 49 (1962).

9 3D-Debye function table: J. A. Beattie, J. Math. Phys. (MIT), 6,1 (1926/27).

10 2D-Debye function table: U. Gaur, G. Pultz, H. Wiedemeier, B. Wunderlich, J. Thermal Anal., 43, 297 (1981).

11 1D-Debye function table: B. Wunderlich, J. Chem. Phys. 37, 1207 (1962).

12 Tarasov equation discussion: V. V. Tarasov, Zh. Fiz. Khim., 24, 1430 (1953); ibid., 39, 2077 (1965); Dokl. Akad. Nauk SSSR 100, 307 (1955).