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CALCULATION OF THE HEAT CAPACITY OF LINEAR MACROMOLECULES FROM THETA-TEMPERATURES AND GROUP VIBRATIONS

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An automated computer program is presented for the calculation of heat capacity of macromolecules from skeletal vibration frequencies described by the Tarasov equation and group vibration frequencies. The heat capacities calculated for crystalline polyethylene and polytetrafluoroethylene fit well with the experimental data from our ATHAS data bank. The program will be part of the planned ATHAS Computation Center.

The Advanced THermal Analysis System (ATHAS)

With the development of differential scanning calorimetry (DSC) and improved electronics, fast, precise thermal analysis became possible. Many heat capacity measurements on macromolecules have been reported as a result. In 1980, an Advanced THermal AnalysiS (ATHAS) laboratory devoted to linear macromolecules was set up. Its goal is to provide a center for measurement, computation, data collection and teaching. The overall structure for this center is outlined in Fig. 1 [1].

The center block, a Heat Capacity Data Center, has been developed since 1963 [2]. It maintains by now a collection of more than 500 publications and 800 heat capacity tables and includes all reported measurements on the heat capacity of polymers. At present, recommended data are available for 96 polymers. All are discussed in nine review articles [3]. One of the main goals of the Computation Center is to properly link heat capacity, which represents a macroscopic description, to the microscopic description. Several computer programs have already been developed which permit an interpretation (inversion) of the heat capacity in terms of vibrational spectra [4]. The reverse calculation, that of the calculation of heat capacities from known vibrational spectra will be presented in this paper.

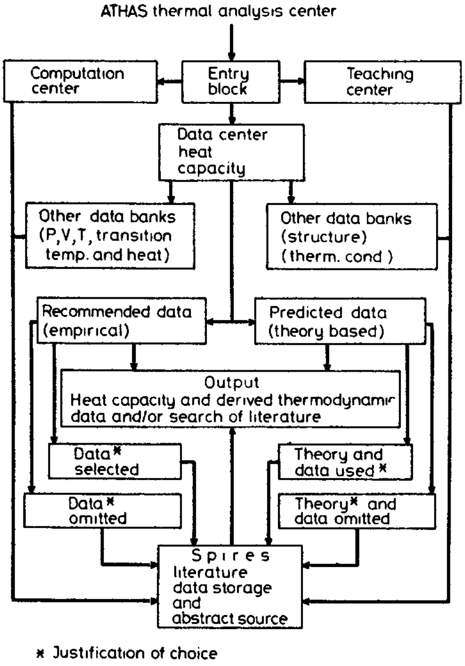

Fig. 1 Block diagram of ATHAS

Computer programs of the Computation Center

All programs of the Computation Center are written in Fortran IV. They are designed to evaluate heat capacities from vibrational frequency spectra or to invert heat capacities to approximate frequency spectra. The presently available programs are listed in Table 1. The first three programs CAP1D, CAP2D and CAP3D are used to find heat capacity (CV/NR) as a function of the theta temperature to temperature ratio (THETA/TEMP) for solids which can be approximated by a one-dimensional, two-dimensional or three-dimensional continuum, respectively. The results from these programs, capable to recalculate heat capacity tables to high precision, have been discussed in ref. [4].

The THETA3 program is used to find the Debye theta-temperature from low temperature heat capacity data. A 3-dimensional continuum of given number of vibrators (N) is assumed. A block diagram of this inversion routine is given in ref. [4]. Such a program is also incorporated in THETA–TAR [4]. THETA–TAR–EB, an updated version of THETA–TAR is used to find the Θ_1 and Θ_2 temperature by using the Tarasov 1, 3 equation with or without prior correction of the heat capacity data for group vibrations.

Table 1 Computer programs for calculation of heat capacity in the Computation Center of ATHAS

Programs	Description
CAP1D[1] CAP2D[1] CAP3D[1]	Calculate *CV/NR* for Debye 1-dimensional, 2-dimensional and 3-dimensional continuum, respectively, for a given Θ/T.
THETA-3[1]	Calculate Θ_D for a 3-dimensional continuum from given heat capacities (inversion).
THETA–TAR–EB[2]	Calculate Θ_1 and Θ_2 for Tarasov equation from given heat capacities (inversion).
CVTOT[3]	Calculate heat capapcity if theta temperatures of skeletal vibrations and the frequency of group vibration are given (Incorporates also CAP1D, CAP2D and CAP3D programs).

[1] See reference [6].

[2] See reference [4] for an earlier version [THETA–TAR] which does not include the use of box distributions for the group vibrations.

[3] Present paper.

Finally, the present CVTOT program is designed to calculate the heat capacity from skeletal modes and group vibrations given as Tarasov functions, Einstein terms or box distributions.

A subroutine contained in all programs is designed to calculate the integrand in the Debye function

$$\int_0^B \frac{x}{\exp(1-x)} dx \tag{1}$$

The program, DO1AGF, is evoked from the NAG Library [5] whenever it is needed in the main program. DO1AGF is utilizing the double-adaptive integration strategy of the Clenshaw–Curtis method [4].

The remainder of the paper will be devoted to the description of the CVTOT program and finally, the application to crystalline polyethylene and polytetrfluoroethylene.

Calculation of heat capacity from theta temperatures and group vibrations

The program (CVTOT) is designed to calculate the heat capacity of linear macromolecules due to the skeletal vibrations and group vibrations. Figure 2 outlines the calculation strategy. The heat capacity contributions from the skeletal vibrations are sorted into seven different cases depending on the given input Θ_1, Θ_2 and Θ_3

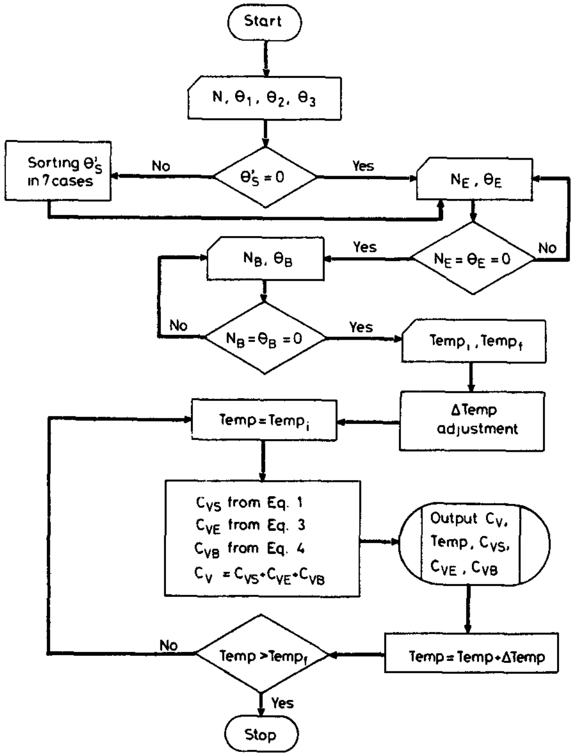

Fig. 2 Block diagram for the calculation of heat capacity using theta temperatures, Einstein frequencies and box frequency distributions

(Tarasov 123, Tarasov 12, Tarasov 13, Tarasov 23, Debye 1, Debye 2 and Debye 3). All cases follow the general format [2]:

$$\begin{aligned}\frac{CV_S}{NR} &= D_1\left(\frac{\Theta_1}{T}\right) - \frac{\Theta_2}{\Theta_1}\left[D_1\left(\frac{\Theta_2}{T}\right) - D_2\left(\frac{\Theta_2}{T}\right)\right] - \\ &- \left(\frac{\Theta_3^2}{\Theta_1\Theta_2}\right)\left[D_2\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right]\end{aligned} \tag{2}$$

The above equation will reduce to the classical Tarasov equation if Θ_2 is set equal to Θ_3.

$$\frac{CV_S}{NR} = D_1\left(\frac{\Theta_1}{T}\right) - \frac{\Theta_3}{\Theta_1}\left[D_1\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right] \tag{3}$$

The other six cases are similarly set by appropriately assigning Θ_1, Θ_2 and Θ_3.

If the full set of actual normal modes of the skeletal vibrations is known, the approximation of eq. (2) can be bypassed ($\Theta's = 0$) and the actual frequencies can be read-in. Their contributions to the heat capacity are then calculated along with the group vibrations using large series of terms of Einstein functions (Θ_E) (eq. (4)) if isolated, narrow distributions of frequencies are present; or by using box distribution functions (Θ_B) (eq. (5)) if there are broader bands of frequencies of constant multiplicity.

$$\frac{CV_E}{NR} = \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right) - 1\right]^2} \tag{4}$$

$$\frac{CV_B}{NR} = \left(\frac{\Theta_U}{\Theta_U - \Theta_L}\right)\left[D_1\left(\frac{\Theta_U}{T}\right) - \left(\frac{\Theta_L}{\Theta_U}\right)D_1\left(\frac{\Theta_L}{T}\right)\right] \tag{5}$$

where subscripts E, L and U represent the Einstein frequency and the lower and upper limit of the frequency distribution, respectively. The corresponding numbers of vibrations N are needed for the program. $N = 1$ for each full normal mode and N = fractional if a normal mode is broken up in partial frequency ranges. The temperature range of calculation from T_i to T_f (in the standard steps established for the ATHAS data bank) completes the input. The computer program, CVTOT, is listed in Appendix 1. It evaluates CV as sum of the skeletal (Tarasov) terms (CV_S), Einstein terms (CV_E) and box distribution terms (CV_B).

Results and discussion

With the computer programs available, a theoretical approach for the discussion of heat capacities is easily available. Crystalline polyethylene, PE, and polytetrafluoroethylene, PTFE, may serve as examples for the application of CVTOT. The skeletal modes described by the Tarasov Θ_1 and Θ_3 are derived by first using the THETA3 program to invert the low temperature heat capacity data. The results for PE and PTFE were $\Theta_D = 235$ K and $\Theta_D = 90$ K, respectively. Then, using the THETA–TAR–EB program, after separating the heat capacity contributions from the group vibrations, Θ_1 and Θ_3 are established ($\Theta_1 = 519$ K and $\Theta_3 = 158$ K for PE and $\Theta_1 = 250$ K and $\Theta_3 = 54$ K for PTFE) [6, 7]. The frequencies of the seven normal modes of the group vibrations of each $-CH_2-$ and $-CF_2-$ (which leave two modes ($N = 2$) for the skeletal vibrations, describable by the Tarasov equation with Θ_1 and Θ_3) were retrieved from the dispersion curves by Kitagawa and Miyazawa for PE [8], and by Hannon et al. for PTFE [9]. Both spectra were calculated for isolated chains.

To judge the constributions of a vibration to the heat capacity, one must remember that low frequency vibrators contribute more significantly to low temperature heat capacity than those with higher frequency. Figure 3 gives some typical examples. The Einstein function reaches full excitation and a heat capacity of 8.3 J/K (for $N = 1$ mole of vibrators) somewhat above the Θ-temperature. At 500 K, for example, vibra-

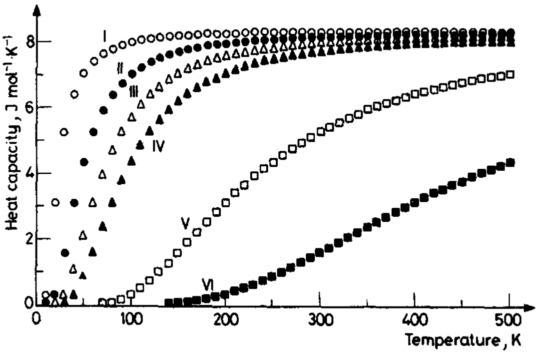

Fig. 3 Heat capacities calculated from Einstein functions of different frequency (for $N = 1$ mole vibrators). Wave numbers used in curves I to VI are 50, 100, 150, 200, 500 and 1000 cm^{-1}, respectively. These correspond to Θ-temperatures of 72, 144, 216, 288, 719 and 1439 K, respectively

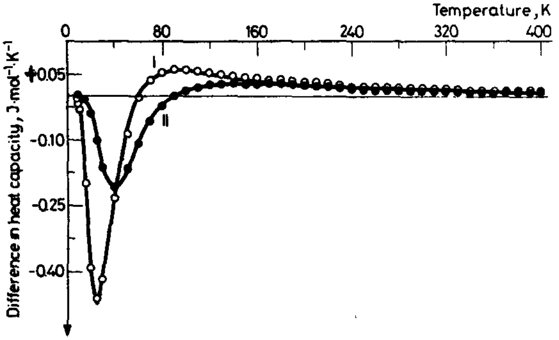

Fig. 4 Difference in heat capacity calculated from an average Einstein function and a box-distribution function [for $N = 1$ mole vibrators; Einstein function = E (frequency); Box-distribution function = B (frequency$_L$, frequency$_U$)]. Curve I. Difference in heat capacity of E (100 cm^{-1}) – B (50 cm^{-1}, 150 cm^{-1}). Curve II. Difference in heat capacity of E (150 cm^{-1}) – B (100 cm^{-1}, 200 cm^{-1}) (to go from cm^{-1} to K multiply with hc/k = = 1.439 K cm)

tors with wave numbers of 1000 cm$-^1$ (1439 K) are only giving half the heat capacity of those with wave numbers of 50–200 cm$-^1$ (70–300 K). Comparing the use of average Einstein functions and box-distributions, one finds that there is little difference in the medium and high temperature range relative to the Θ-temperatures involved. However, there is a significant difference in the lower temperature range, as is demonstrated in Fig. 4. Two sets of heat capacity differences between data calculated from an average Einstein function and a corresponding box distribution are plotted as a function of temperature. The width of the box distributions is kept to 100 cm$-^1$, which is the typical range of broader group vibrations. Both curves

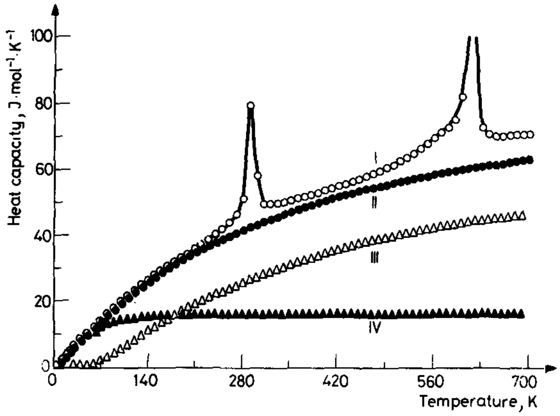

Fig. 5 Heat capacity at constant volume of crystalline polytetrafluoroethylene. Curve I. Heat capacity at constant pressure from ATHAS data bank. Curve II. Calculated heat capacity at constant volume (III + IV) with CVTOT. Curve III. Calculated heat capacity contribution from group vibrations only. Curve IV. Calculated heat capacity from skeletal vibrations only (Tarasov theta-1 and theta-3)

show a minimum in the temperature range from 25 to 50 K (i.e. low frequencies of the box distribution contribute more to the heat capacity than the average Einstein function). This minimum becomes smaller and moves to higher temperature as the frequency limits increase. The minima of curves I and II, appearing at 25 and 40 K, would involve errors of 52.4 and 18.5% in heat capacity, respectively, if the Einstein calculation were used instead of the box distribution (compare to Fig. 3). As the temperature increases, the Einstein function becomes larger and finally both methods give almost the same result (at 250 K the difference is only 0.085%).

The heat capacities of crystalline PE and PTFE at constant volume were calculated from 0 to 460 K and 0–700 K, respectively, using the CVTOT program. The results are plotted in Figs 5 and 6. It is clear from these figures that the agreement between theory (curves II) and experiment (curves I) is rather good in the temperature region of 0.5–150 K. Above 150 K, comparisons to the experiments are more difficult. In PTFE there is the beginning of the room temperature crystal-crystal transition. In both polymers the difference of heat capacity at constant pressure and constant volume becomes noticeable in this temperature range. In PE the experimentally derived steep increase above 350 K cannot be due to the vibrational frequencies being excited, rather it may be due to increasing defect formation [10]. The contribution of skeletal vibrations (curves IV) and of the group vibrations (curves III) to the heat capacity are also shown separately in Figs 5 and 6. The skeletal vibrations of PTFE are completely excited much before those of PE and the group vibrations also begin earlier to contribute to the heat capacity for PTFE. The main reason for this higher heat capacity of PTFE at low temperature is the greater mass of F relative to H.

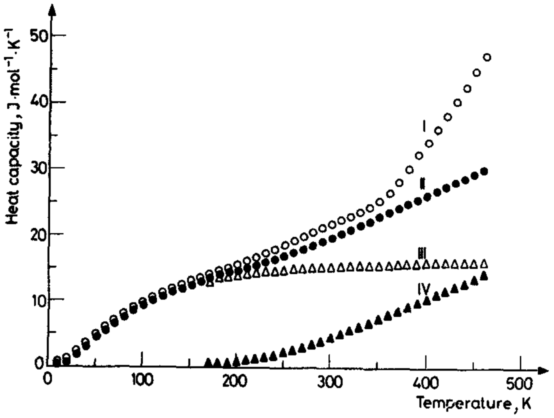

Fig. 6 Heat capacity at constant volume of crystalline polyethylene. Curve I. Heat capacity at constant pressure from ATHAS data bank. Curve II. Calculated heat capacity at constant volume (III + IV) with CVTOT. Curve III. Calculated heat capacity contribution from group vibrations only. Curve IV. Calculated heat capacity from skeletal vibrations only (Tarasov theta-1 and theta-3)

The heat capacity of crystalline PTFE was also calculated directly from the frequency spectrum of the isolated chain given in ref. [9] (44 terms of Einstein frequencies for the two skeletal vibrations and the same set of frequencies for the group vibrations as before). The calculated heat capacity does not agree at low temperature with the measurements. At 0.3 K, for example, the calculations are 1000 times bigger than the experimental data, and at 5 K they are still about 10 times bigger. Such huge discrepancies arise when intermolecular interactions between the polymer chains are neglected.

The heat capacity at constant volume can be recalculated to values at constant pressure using either the Nernst–Lindemann equation:

$$C_p = C_v + \frac{AC_p^2 T}{T_m} \tag{6}$$

with A representing a constant, or the general thermodynamic function:

$$C_p = C_v + \frac{\alpha^2 TV}{\beta} \tag{7}$$

with α representing the expansivity and β the compressibility. Since experimental data for α and β are frequently not available for the whole temperature range, we derived from limited information values for A. For PE a value of A of $4.85 \cdot 10^{-3}$ K mol/J was proposed [10] and for PTFE A is $1.62 \cdot 10^{-3}$ K mol/J [7]. For PTFE this value makes the calculations fit the measurements well [7], for PE some problems remain [10].

A major benefit of the konwledge of theory backed heat capacities is the ability to then discuss heats of transitions of broad transformation ranges. From Fig. 5 one can see that both the melting and the room temperature transition of PTFE are over 100 K wide.

Conclusions

This study presents computer programs for the calculation of heat capacity from the Tarasov Θ temperatures and group vibration frequencies. It demonstrates the application to polyethylene and polytetrafluoroethylene. Using theory backed heat capacities, it is possible to arrive at a better knowledge of broad range transitions which are common in macromolecules.

* * *

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A-1

Appendix 1.

Computer Program (CVOT) for the calculation of heat capacity from theta temperatures, Einstein frequencies and box distribution frequencies.

```
C          ****************************************
C          *                                      *
C          *     CALCULATIONS OF HEAT CAPACITY    *
C          *        FROM THETA TEMPERATURES       *
C          *          EINSTEIN THETAS AND         *
C          *           BOX DISTRIBUTIONS          *
C          *                                      *
C          ****************************************
C
C  The variables used in this program are kept the same as
C  those in the 'THETA3' and 'THETA-TAR'
C  programs, except for those which are stated below.
C
C  BBU, BBL --- upper limit for the integrals for the box
C               distribution at both ends
C  BSUM     --- total heat capacity calculated from the box
C               distribution term(s) at a given temperature
C  CV       --- heat capacity calculated solely from the
C               skeletal vibration(s) of the backbone at a
C               given temperature
C  DTEMP    --- temperature under consideration
C  ICASE    --- different routes of calculating the heat
C               capacity from the skeletal vibrations which
C               depend on the three input theta temperatures.
C               They are assigned the numerals from 1 to 7
C               which corrspond to Tarasov 123, Tarasov23,
C               Tarasov 13, Tarasov 12, Debye 3, Debye 2 and
C               Debye 1, respectively
C  JB       --- total number of the input theta temperature
C               pairs for the box distributions
C  KIND,    --- types of the theta temperature(s) that
C    KINDB,     contribute to the overall heat capacity.
C   KINDE       They are theta temperature(s) due to the
C               skeletal vibration(s), theta(s) due to the
C               box distribution(s) and theta(s) due to the
C               Einstein term(s), respectively
C  LTEMP,   --- lower and upper temperature range for the
C    UTEMP      output heat capacity
C  LTHETA,  --- lower and upper input theta temperatures
C    UTHETA     for the individual box distributions
C  NB, NE   --- number of moles of vibrators which have the
C               same range of frequency or the same frequency,
C               respectively.  The first refers to a box dis-
C               tribution while the latter one for an Ein-
C               Einstein term
C  RANGE    --- different intervals in the input temperature
C               range <LTEMP, UTEMP>.  They are assigned the
C               numerals from 1 to 5 which corresponds to the
C               intervals of <0, 1>, <1, 2>, <3, 10>, <15, 30>
C               and <30, 1000>, respectively
```

A-2

```
C  TOTAL     --- overall heat capacity generated from the box
C                distribution(s), Einstein term(s) and the
C                skeletal theta temperature(s)
C  UPPER     --- the highest limit of the output temperature
C                which is a multiple of ten for calculating
C                the heat capacity
C
C ***********************************************************
C
      INTEGER  RANGE
      LOGICAL*1  NAME(70)
      REAL*8  DTEMP, CV, THETA1, THETA2, THETA3, B1, B2, B3,
     *      R, REAL, RAT21, RAT31, RAT32, RAT321, PI, NE(1000),
     *      DEBY11, DEBY12, DEBY13, DEBY22, DEBY23, DEBY33,
     *      THETAE(1000), SUM, TOTAL, X(1000), Y(1000), CVE(1000),
     *      LTHETA(1000), UTHETA(1000), BRAT1(1000), BRAT2(1000),
     *      BBU(1000), BBL(1000), CVB(1000), DEBYU(1000),
     *      DEBYL(1000), BSUM, BCONST(1000), NB(1000)
C
C     Initialization of constants and variables
C
      R = 8.31434D0
      PI = 3.141593D0
      KIND = 0
      KINDE = 0
      KINDB = 0
      K = 1
      J = 1
      KK = 1
      JB = 1
      CV = 0.0D0
      SUM = 0.0D0
      BSUM = 0.0D0
      TOTAL = 0.0D0
C
C     Obtain the name of polymer, number of vibrators per
C     repeating unit and the theta temperatures due to the
C     skeletal vibrations of the backbone.  The above
C     information is printed according to the preset format
C
      READ (5, 1000) (NAME(II), II=1,70), N, THETA1, THETA2,
     *      THETA3
      REAL = N*R
      WRITE (6, 3000) (NAME(II), II=1, 70), N, THETA1,
     *      THETA2, THETA3
C
C     If the input skeletal theta(s) are not all equal to
C     zero, the program will go to the subprogram 'CASE' to
C     sort out the theta(s) into eight different cases --
C     'ICASE'
```

A-3

```
      IF (THETA1 .EQ. 0.0D0 .AND. THETA2 .EQ. 0.0D0 .AND.
     *   THETA3 .EQ. 0.0D0) GOTO 600
       KIND = 1
       CALL CASE(THETA1, THETA2, THETA3, ICASE, RAT21,
     *      RAT321, RAT32, RAT31)
C
C     Obtain the value for the total number of moles of
C     vibrators that have the same vibrational frequency and
C     its corresponding theta temperature for the Einstein
C     term(s).  The counter is used so that the total
C     number of different Einstein terms are determined.
C     A list of all the given terms are printed after they
C     have been read
C
 600  READ (5, 4000) NE(K), THETAE(K)
      IF (NE(K) .EQ. 0 .AND. THETAE(K) .EQ. 0.0D0) GOTO 605
       KINDE = 1
       DO 500 K = 2, 1000
        READ (5, 4000) NE(K), THETAE(K)
        IF (NE(K) .EQ. 0 .AND. THETAE(K) .EQ. 0.0D0)
     *       GOTO 620
         J = J + 1
 500   CONTINUE
C
 620  IF (J .EQ. 1) GOTO 621
       WRITE (6, 5000) (NE(K), THETAE(K), K=1,1)
       JJ = J - 2
       IF (JJ .EQ. 0) GOTO 622
        JJJ = J - 1
        DO 623 K = 2, JJJ
         WRITE (6, 5010) NE(K), THETAE(K)
 623    CONTINUE
C
 622   WRITE (6, 5020) (NE(K), THETAE(K), K=J,J)
       GOTO 605
 621  WRITE (6, 5030) (NE(K), THETAE(K), K=1,1)
C
C     The logic of the following section is similiar to the
C     previous explanation note, except this section is re-
C     lated to the box distribution terms
C
 605  READ (5, 4050) NB(KK), LTHETA(KK), UTHETA(KK)
      IF (NB(KK) .EQ. 0 .AND. UTHETA(KK) .EQ. 0.0D0 .AND.
     *   LTHETA(KK) .EQ. 0.0D0) GOTO 610
       KINDB = 1
       DO 554 KK = 2, 1000
        READ (5, 4050) NB(KK), LTHETA(KK), UTHETA(KK)
        IF (NB(KK) .EQ. 0 .AND. UTHETA(KK) .EQ. 0.0D0
     *     .AND. LTHETA(KK) .EQ. 0.0D0) GOTO 630
         JB = JB + 1
```

```
 554    CONTINUE
C
 630  IF (JB .EQ. 1) GOTO 631
        WRITE (6, 5050) (NB(L), LTHETA(L), UTHETA(L), L=1,1)
        JJB = JB - 2
        IF (JJB .EQ. 0) GOTO 632
          JJJB = JB - 1
          DO 633 L = 2, JJJB
            WRITE (6, 5060) NB(L), LTHETA(L), UTHETA(L)
 633      CONTINUE
C
 632    WRITE (6, 5070) (NB(L), LTHETA(L), UTHETA(L),
     *          L=JB,JB)
        GOTO 610
 631  WRITE (6, 5080) (NB(L), LTHETA(L), UTHETA(L), L=1,1)
C
C     Obtain the temperature range for the heat capacity
C     calculation.  Next, output the above information and
C     then sort out the temperature range so that the
C     correct increment of temperature is added to the
C     previous temperature before the next calculation is
C     executed.  After the temperature range is defined,
C     the heat capacity due to the skeletal modes is
C     evaluated (using either the Tarasov or Debye equations)
C     by following the route which is governed by 'ICASE'
C
 610  READ (5, 2000) LTEMP, UTEMP
      WRITE (6, 6000) LTEMP, UTEMP
      IUTEMP = UTEMP * 10.0 + 0.4
      IUREM = MOD(IUTEMP, 100)
      IF (IUREM .EQ. 0) GOTO 35
        XX = 10.0 - FLOAT(IUREM)/10.0
        UPPER = UTEMP + XX + 0.4
        GOTO 36
 35   UPPER = UTEMP
C
 36   TEMP = LTEMP
      ILTEMP = TEMP * 10.0 + 0.4
      IF (TEMP .GT. 1.0) GOTO 50
        RANGE = 1
 40     IF (KIND .EQ. 0) GOTO 520
        GOTO (700, 820, 840, 860, 920, 940, 960), ICASE
 41     TEMP = TEMP + 0.1
        IF (TEMP .LE. 1.0) GOTO 40
          RANGE = 2
          TEMP = TEMP + 0.1
 42       IF (KIND .EQ. 0) GOTO 520
            GOTO (700, 820, 840, 860, 920, 940, 960), ICASE
 43       TEMP = TEMP + 0.2
          IF (TEMP .LE. 2.0) GOTO 42
```

```
            RANGE = 3
            TEMP = TEMP + 0.8
 44         IF (KIND .EQ. 0) GOTO 520
              GOTO (700, 820, 840, 860, 920, 940, 960),
     *                ICASE
 45         TEMP = TEMP + 1.0
            IF (TEMP .LE. 10.0) GOTO 44
              RANGE = 4
              TEMP = TEMP + 4.0
 46           IF (KIND .EQ. 0) GOTO 520
                GOTO (700, 820, 840, 860, 920, 940, 960),
     *                  ICASE
 47           TEMP = TEMP + 5.0
              IF (TEMP .LE. 30.0) GOTO 46
                RANGE = 5
                TEMP = TEMP + 5.0
 48             IF (KIND .EQ. 0) GOTO 520
                  GOTO (700, 820, 840, 860, 920, 940, 960),
     *                    ICASE
 49             TEMP = TEMP + 10.0
                IF (TEMP .LE. UPPER) GOTO 48
                  GOTO 999
C
 50   IF (TEMP .GT. 2.0) GOTO 60
        IREM2 = MOD(ILTEMP, 2)
        IF (IREM2 .EQ. 0) GOTO 51
          TEMP = TEMP - 0.1
 51     RANGE = 2
        GOTO 42
C
 60   IF (TEMP .GT. 10.0) GOTO 70
        IREM3 = MOD(ILTEMP, 10)
        IF (IREM3 .EQ. 0) GOTO 61
          YY = FLOAT(IREM3)/10.0
          TEMP = LTEMP - YY
 61     RANGE = 3
        GOTO 44
C
 70   IF (TEMP .GT. 30.0) GOTO 80
        IREM4 = MOD(ILTEMP, 50)
        IF (IREM4 .EQ. 0) GOTO 71
          ZZ = FLOAT(IREM4)/10.0
          TEMP = TEMP - ZZ
 71     RANGE = 4
        GOTO 46
C
 80   IREM5 = MOD(ILTEMP, 100)
      IF (IREM5 .EQ. 0) GOTO 81
        WW = FLOAT(IREM5)/10.0
        TEMP = TEMP - WW
```

```
 81   RANGE = 5
      GOTO 48
C
C     The following section is used to calculate the heat
C     capacity of a Tarasov 123 system due to the skeletal
C     vibrations by using five different subprograms, 'CV'
C     After it has been found, the program will proceed to
C     the next step for finding the heat capacity from the
C     Einstein term(s)
C
 700  DTEMP = DBLE(TEMP)
      B1 = THETA1/DTEMP
      B2 = THETA2/DTEMP
      B3 = THETA3/DTEMP
      CALL CV1(B1, PI, DEBY11)
      CALL CV1(B2, PI, DEBY12)
      CALL CV2(B2, DEBY22)
      CALL CV2(B3, DEBY23)
      CALL CV3(B3, PI, DEBY33)
      CV = REAL*DEBY11 - REAL*RAT21*(DEBY12 - DEBY22)
     *                   - REAL*RAT321*(DEBY23 - DEBY33)
      GOTO 520
C
C     Calculate the heat capacity for a Tarasov 23 system
C
 820  DTEMP = DBLE(TEMP)
      B2 = THETA2/DTEMP
      B3 = THETA3/DTEMP
      CALL CV2(B2, DEBY22)
      CALL CV2(B3, DEBY23)
      CALL CV3(B3, PI, DEBY33)
      CV = REAL*(DEBY22 - RAT32*(DEBY23 - DEBY33))
      GOTO 520
C
C     Calculate the heat capacity for a Tarasov 13 system
C
 840  DTEMP = DBLE(TEMP)
      B1 = THETA1/DTEMP
      B3 = THETA3/DTEMP
      CALL CV1(B1, PI, DEBY11)
      CALL CV1(B3, PI, DEBY13)
      CALL CV3(B3, PI, DEBY33)
      CV = REAL*(DEBY11 - RAT31*(DEBY13 - DEBY33))
      GOTO 520
C
C     Calculate the heat capacity for a Tarasov 12 system
C
 860  DTEMP = DBLE(TEMP)
      B1 = THETA1/DTEMP
      B2 = THETA2/DTEMP
```

A-7

```
      CALL CV1(B1, PI, DEBY11)
      CALL CV1(B2, PI, DEBY12)
      CALL CV2(B2, DEBY22)
      CV = REAL*(DEBY11 - RAT21*(DEBY12 - DEBY22))
      GOTO 520
C
C     Calculate the heat capacity for a Debye 3 system
C
 920  DTEMP = DBLE(TEMP)
      B3 = THETA3/DTEMP
      CALL CV3(B3, PI, DEBY33)
      CV = REAL*DEBY33
      GOTO 520
C
C     Calculate the heat capacity for a Debye 2 system
C
 940  DTEMP = DBLE(TEMP)
      B2 = THETA2/DTEMP
      CALL CV2(B2, DEBY22)
      CV = REAL*DEBY22
      GOTO 520
C
C     Calculate the heat capacity for a Debye 1 system
C
 960  DTEMP = DBLE(TEMP)
      B1 = THETA1/DTEMP
      CALL CV1(B1, PI, DEBY11)
      CV = REAL*DEBY11
      GOTO 520
C
C     Find the heat capacity from the input Einstein theta(s)
C     and the related number of mole of vibrator.  If no
C     Einstein theta(s) are given, this section will be by-
C     passed and the program will go directly to the next
C     section
C
 520  DTEMP = DBLE(TEMP)
      IF (KINDE .EQ. 0) GOTO 530
        DO 550 M = 1, J
          X(M) = THETAE(M)/DTEMP
          IF (X(M) .GT. 7.5D01) GOTO 560
            Y(M) = DEXP(X(M)).
            GOTO 570
 560      CVE(M) = 0.0D0
          GOTO 580
 570      CVE(M) = NE(M)*R*X(M)**2*Y(M)/(Y(M)-1.0D0)
     *                                       /(Y(M)-1.0D0)
 580    SUM = SUM + CVE(M)
 550    CONTINUE
C
```

A-8

```
C     Calculate the heat capacity from the two ends of the
C     individual box distribution region.  Subprogram CV1
C     is used to find all the required values.  The heat
C     capacity from each box distribution is added together
C     to give a total value.  If no input region is given,
C     this section will be bypassed.
C
 530  DTEMP = DBLE(TEMP)
      IF (KINDB .EQ. 0) GOTO 9000
        DO 555 MM = 1, JB
          BRAT1(MM) = UTHETA(MM)/(UTHETA(MM) - LTHETA(MM))
          BRAT2(MM) = LTHETA(MM)/UTHETA(MM)
          BBU(MM) = UTHETA(MM)/DTEMP
          BBL(MM) = LTHETA(MM)/DTEMP
          IF (BBU(MM) .GT. 20.0D0 .AND. BBL(MM) .GT. 20.0D0)
     *               GOTO 535
            CALL CV1(BBU(MM), PI, DEBYU(MM))
            CALL CV1(BBL(MM), PI, DEBYL(MM))
            BCONST(MM) = NB(MM)*R*BRAT1(MM)
            CVB(MM) = BCONST(MM)*(DEBYU(MM)
     *                                - BRAT2(MM)*DEBYL(MM))
            GOTO 536
 535      CVB(MM) = 0.0D0
 536      BSUM = BSUM + CVB(MM)
 555    CONTINUE
C
C     Add up all heat capacities from the three different
C     sources (skeletal vibrations, Einstein terms and
C     box distributions).  Then this value, together with
C     the temperature and the heat capacity from each
C     source are printed according to the preset format.
C     Before going back to obtain the next temperature
C     value, all the variables related to the heat capacity
C     are reset to zero.
C
 9000 TOTAL = CV + SUM + BSUM
      WRITE (6, 7000) TEMP, CV, SUM, BSUM, TOTAL
      CV = 0.0D0
      SUM = 0.0D0
      BSUM = 0.0D0
      TOTAL = 0.0D0
      GOTO (41, 43, 45, 47, 49), RANGE
C
 1000 FORMAT (70A1/I2, 2X, F6.1, 2X, F6.1, 2X, F6.1)
 2000 FORMAT (F6.1, 2X, F6.1)
 3000 FORMAT ('1'/'-'/'-', 30X, 'CALCULATION OF HEAT
     *       CAPACITY'/33X, 'USING THETA TEMPERATURES'/'-',
     *       4X, 70A1/'0', 42X, 'N = ', I2/'0',18X, 'Theta
     *       Temperatures (1, 2, 3) = (', 2(F6.1, ', '),
     *       F6.1, ')'/' ')
```

A-9

```
 4000 FORMAT (F7.4, 2X, F6.1)
 4050 FORMAT (F7.4, 2X, F6.1, 2X, F6.1)
 5000 FORMAT (18X, 'Einstein Temperatures (N, Theta) = (',
     *       F7.4, ', ', F6.1, '),')
 5010 FORMAT (53X, '(', F7.4, ', ', F6.1, '),')
 5020 FORMAT (53X, '(', F7.4, ', ', F6.1, ').'/' ')
 5030 FORMAT (18X, 'Einstein Temperatrues (N, Theta) = (',
     *       F7.4, ', ', F6.1, ').'/' ')
 5050 FORMAT (10X, 'Box Distributions (N, Theta-L, Theta-U)',
     *       ' = (', F7.4, ', ', F6.1, ', ', F6.1, '),')
 5060 FORMAT (52X, '(', F7.4, ', ', F6.1, ', ', F6.1, '),')
 5070 FORMAT (52X, '(', F7.4, ', ', F6.1, ', ', F6.1, ').')
 5080 FORMAT (10X, 'Box Distributions (N, Theta-L, Theta-U)',
     *       ' = (', F7.4, ', ', F6.1, ', ', F6.1, ').')
 6000 FORMAT ('0', 22X, 'Output Temperature Range = (',
     *       F5.1, ', ', F6.1, ')'/'1'/'-', 10X, 'Temp', 7X,
     *       'Cv(S)', 10X, 'Cv(E)', 10X, 'Cv(B)', 10X, 'Cv'/
     *       ' ')
 7000 FORMAT (9X, F6.1, 2X, E13.6, 2X, E13.6, 2X, E13.6, 2X,
     *       E13.6)
C
 999  STOP
      END
C
C
C ********************************************************
C
           SUBROUTINE CASE(THETA1, THETA2, THETA3, ICASE,
     *                RAT21, RAT321, RAT32, RAT31)
C
C ********************************************************
C
      REAL*8  THETA1, THETA2, THETA3, RAT21, RAT321, RAT32,
     *        RAT31
C
      I = 0
C
      IF (THETA1 .NE. 0.0D0) GOTO 10
        I = I + 1
 10     IF (THETA2 .NE. 0.0D0) GOTO 20
          I= I + 1
 20       IF (THETA3 .NE. 0.0D0) GOTO 30
            I = I + 1
C
 30   IF (I .EQ. 3) GOTO 995
        IF (I .EQ. 2) GOTO 900
          IF (I .EQ. 1) GOTO 800
            IF (THETA1 .GT. THETA2 .AND. THETA2 .GT. THETA3)
     *               GOTO 690
            GOTO 995
```

```
 800  IF (THETA1 .EQ. 0.0D0 .AND. THETA2 .GT. THETA3)
     *         GOTO 810
        IF (THETA2 .EQ. 0.0D0 .AND. THETA1 .GT. THETA3)
     *         GOTO 830
          IF (THETA3 .EQ. 0.0D0 .AND. THETA1 .GT. THETA2)
     *         GOTO 850
            GOTO 995
C
 900  IF (THETA1 .EQ. 0.0D0 .AND. THETA2 .EQ. 0.0D0)
     *         GOTO 910
        IF (THETA1 .EQ. 0.0D0 .AND. THETA3 .EQ. 0.0D0)
     *         GOTO 930
           GOTO 950
C
 690  ICASE = 1
      RAT21 = THETA2/THETA1
      RAT321 = THETA3**2/THETA1/THETA2
      GOTO 995
C
 810  ICASE = 2
      RAT32 = (THETA3/THETA2)**2
      GOTO 995
C
 830  ICASE = 3
      RAT31 = THETA3/THETA1
      GOTO 995
C
 850  ICASE = 4
      RAT21 = THETA2/THETA1
      GOTO 995
C
 910  ICASE = 5
      GOTO 995
C
 930  ICASE = 6
      GOTO 995
C
 950  ICASE =7
C
 995  RETURN
      END
C
C
C ***********************************************************
C
      SUBROUTINE CV1(B, PI, DEBY1)
C
C ***********************************************************
C
      REAL*8  B, ANS1, DEBY1, PI
```

```
      IF (B .GT. 20.0D0) GOTO 101
         IF (B .LE. 1.0D-15) GOTO 111
            CALL INT1(B, ANS1)
            GOTO 121
 111     ANS1 = 0.0D0
 121     DEBY1 = 2.0D0/B*ANS1 - B/(DEXP(B)-1.0D0)
         GOTO 131
 101  DEBY1 = PI**2/3.0D0/B
 131  RETURN
      END
C
C
C ***********************************************************
C
      SUBROUTINE CV2(B, DEBY2)
C
C ***********************************************************
C
      REAL*8  B, ANS2, DEBY2
C
      IF (B .GT. 20.0D0) GOTO 201
         IF (B .LE. 1.0D-15) GOTO 211
            CALL INT2(B, ANS2)
            GOTO 221
 211     ANS2 = 0.0D0
 221     DEBY2 = 6.0D0/B**2*ANS2 - 2.0D0*B/(DEXP(B)-1.0D0)
         GOTO 231
 201  DEBY2 = 1.44246828D1*B**(-2)
 231  RETURN
      END
C
C
C ***********************************************************
C
      SUBROUTINE CV3(B, PI, DEBY3)
C
C ***********************************************************
C
      REAL*8  B, ANS3, DEBY3, PI
C
      IF (B .GT. 25.0D0) GOTO 301
         IF (B .LE. 1.0D-15) GOTO 311
            CALL INT3(B, ANS3)
            GOTO 321
 311     ANS3 = 0.0D0
 321     DEBY3 = 12.0D0/B**3*ANS3 - 3.0D0*B/(DEXP(B)-1.0D0)
         GOTO 331
 301  DEBY3 = 4.0D0/5.0D0*PI**4*B**(-3)
 331  RETURN
      END
```

```
C *******************************************************
C
      SUBROUTINE INT1(B, ANS1)
C
C *******************************************************
C
      REAL*8  A, B, EPS, ACC, ANS1, ERROR, FUN1
      EXTERNAL FUN1
C
      A = 1.0D-15
      MAXDIV = 40
      EPS = 1.0D-6
      ACC = 0.0D0
      IFAIL = 1
C
      CALL D01AGF(A, B, FUN1, MAXDIV, EPS, ACC, ANS1, ERROR,
     *   NOFUN, IFAIL)
      RETURN
      END
C
C              *************************
C
C                   FUNCTION FUN1(X)
C
C              *************************
C
      REAL FUNCTION FUN1(X)
      REAL*8  X
      FUN1 = X/(DEXP(X) - 1.0D0)
      RETURN
      END
C
C
C *******************************************************
C
      SUBROUTINE INT2(B, ANS2)
C
C *******************************************************
C
      REAL*8  A, B, EPS, ACC, ANS2, ERROR, FUN2
      EXTERNAL FUN2
C
      A = 1.0D-15
      MAXDIV = 40
      EPS = 1.0D-6
      ACC = 0.0D0
      IFAIL = 1
C
      CALL D01AGF(A, B, FUN2, MAXDIV, EPS, ACC, ANS2, ERROR,
     *   NOFUN, IFAIL)
```

```
      RETURN
      END
C
C               *************************
C
C                    FUNCTION FUN2(X)
C
C               *************************
C
      REAL FUNCTION FUN2(X)
      REAL*8  X
      FUN2 = X**2/(DEXP(X) - 1.0D0)
      RETURN
      END
C
C
C *********************************************************
C
      SUBROUTINE INT3(B, ANS3)
C
C *********************************************************
C
      REAL*8  A, B, EPS, ACC, ANS3, ERROR, FUN3
      EXTERNAL FUN3
C
      A = 1.0D-15
      MAXDIV = 40
      EPS = 1.0D-6
      ACC = 0.0D0
      IFAIL = 1
C
      CALL D01AGF(A, B, FUN3, MAXDIV, EPS, ACC, ANS3, ERROR,
     *   NOFUN, IFAIL)
      RETURN
      END
C
C               *************************
C
C                    FUNCTION FUN3(X)
C
C               *************************
C
      REAL FUNCTION FUN3(X)
      REAL*8  X
      FUN3 = X**3/(DEXP(X) - 1.0D0)
      RETURN
      END
```

A-14

SAMPLE INPUTFILE AND OUTPUT FOR A RECENT CALCULATION FOR POLYOXYMETHYLENE

[Note proper line numbers and column numbers: 1 general title of calculation; 2 number of modes (N=2) and various theta temperatures (Θ_1 = 222.2, Θ_2 = 0.0, Θ_3 = 119.6); 4 to 16 number of Einstein modes (N=0.23, 1.0, 1.0, 0.22 ....) and Θ_E-temperatures in K (655.0, 869.7, 1304.6, 1385.1....); 19-24 box distributions characterized by N (0.32 ...) Θ_L (162.3 ...) and Θ_U (319.1); 25 lowest temperature of calculation T_L and highest temperature of calculation T_D].

```
  1     POM-cr(Apr.15,1983).Data after Boeiro +Theta 1,Theta 3.CVTOT.
  2     02   222.2     0.0   119.6
  4      0.23      655.0
  5      1.0       869.7
  6      1.0      1304.6
  7      0.22     1385.1
  8      0.11     1632.1
  9      0.2      1524.7
 10      0.24     1707.2
 11      1.0      1921.9
 12      1.0      2018.6
 13      1.0      2050.8
 14      1.0      2158.2
 15      1.0      4226.5
 16      0.0         0.0
 19      0.32      162.3    319.1
 20      0.29      359.7    440.2
 22      0.67     1385.1   1632.1
 23      0.56     1524.7   1707.2
 24      0.0         0.0      0.0
 25        0.1    550.0
End of file
```

```
                                                              A-15

                              SAMPLE  OUTPUT
                             POLYOXYMETHYLENE


                       CALCULATION OF HEAT CAPACITY
                         USING THETA TEMPERATURES

                           A.  Input Verification


POM-cr(Apr.15,1983).Data after Boeiro +Theta 1,Theta 3.CVTOT.

                                 N =  2

             Theta Temperatures (1, 2, 3) = ( 222.2,    0.0,  119.6)

            Einstein Temperatures (N, Theta) = ( 0.2300,  655.0),
                                               ( 1.0000,  869.7),
                                               ( 1.0000, 1304.6),
                                               ( 0.2200, 1385.1),
                                               ( 0.1100, 1632.1),
                                               ( 0.2000, 1524.7),
                                               ( 0.2400, 1707.2),
                                               ( 1.0000, 1921.9),
                                               ( 1.0000, 2018.6),
                                               ( 1.0000, 2050.8),
                                               ( 1.0000, 2158.2),
                                               ( 1.0000, 4226.5).

     Box Distributions (N, Theta-L, Theta-U) = ( 0.3200,  162.3,  319.1),
                                               ( 0.2900,  359.7,  440.2),
                                               ( 0.6700, 1385.1, 1632.1),
                                               ( 0.5600, 1524.7, 1707.2).

                 Output Temperature Range = (  0.1,  550.0)
```

```
                                                          A-16

                              DATA OUTPUT
(Cv(S)=Skeletal contribution (eq. 3);  Cv(E)=Group contributions
from Einstein terms (eq. 4);  Cv(B)=Group contributions from box
distributions (eq. 5);  Cv=Total heat capacity; sum:  S + E + B)


Temp       Cv(S)           Cv(E)            Cv(B)            Cv

  0.1   0.407701E-06   0.0             0.0             0.407701E-06
  0.2   0.326160E-05   0.0             0.0             0.326160E-05
  0.3   0.110079E-04   0.0             0.0             0.110079E-04
  0.4   0.260928E-04   0.0             0.0             0.260928E-04
  0.5   0.509625E-04   0.0             0.0             0.509625E-04
  0.6   0.880632E-04   0.0             0.0             0.880632E-04
  0.7   0.139841E-03   0.0             0.0             0.139841E-03
  0.8   0.208742E-03   0.0             0.0             0.208742E-03
  0.9   0.297213E-03   0.0             0.0             0.297213E-03
  1.0   0.407700E-03   0.0             0.0             0.407700E-03
  1.2   0.704504E-03   0.0             0.0             0.704504E-03
  1.4   0.111873E-02   0.0             0.0             0.111873E-02
  1.6   0.166994E-02   0.0             0.0             0.166994E-02
  1.8   0.237770E-02   0.0             0.0             0.237770E-02
  2.0   0.326159E-02   0.0             0.0             0.326159E-02
  3.0   0.110079E-01   0.0             0.0             0.110079E-01
  4.0   0.260928E-01   0.0             0.0             0.260928E-01
  5.0   0.509624E-01   0.0             0.0             0.509624E-01
  6.0   0.880624E-01   0.0             0.0             0.880624E-01
  7.0   0.139826E+00   0.0             0.0             0.139826E+00
  8.0   0.208620E+00   0.0             0.0             0.208620E+00
  9.0   0.296614E+00   0.250355E-27    0.935690E-06    0.296615E+00
 10.0   0.405565E+00   0.293590E-24    0.463123E-05    0.405569E+00
 15.0   0.127877E+01   0.395970E-15    0.716304E-03    0.127948E+01
 20.0   0.257829E+01   0.122715E-10    0.852692E-02    0.258682E+01
 25.0   0.405296E+01   0.549865E-08    0.366391E-01    0.408960E+01
 30.0   0.551665E+01   0.302192E-06    0.953469E-01    0.561199E+01
 40.0   0.808172E+01   0.410776E-04    0.309403E+00    0.839116E+01
 50.0   0.100463E+02   0.741438E-03    0.622603E+00    0.106696E+02
 60.0   0.114924E+02   0.502413E-02    0.989984E+00    0.124874E+02
 70.0   0.125520E+02   0.196443E-01    0.137402E+01    0.139456E+02
 80.0   0.133362E+02   0.545420E-01    0.174862E+01    0.151393E+02
 90.0   0.139256E+02   0.120428E+00    0.209832E+01    0.161444E+02
100.0   0.143764E+02   0.226332E+00    0.241598E+01    0.170187E+02
110.0   0.147270E+02   0.378252E+00    0.270003E+01    0.178052E+02
120.0   0.150039E+02   0.579000E+00    0.295242E+01    0.185354E+02
130.0   0.152260E+02   0.828792E+00    0.317705E+01    0.192319E+02
140.0   0.154065E+02   0.112610E+01    0.337878E+01    0.199113E+02
150.0   0.155548E+02   0.146845E+01    0.356272E+01    0.205860E+02
160.0   0.156782E+02   0.185303E+01    0.373381E+01    0.212650E+02
170.0   0.157817E+02   0.227706E+01    0.389653E+01    0.219553E+02
180.0   0.158695E+02   0.273799E+01    0.405472E+01    0.226622E+02
190.0   0.159444E+02   0.323357E+01    0.421153E+01    0.233895E+02
200.0   0.160089E+02   0.376183E+01    0.436940E+01    0.241401E+02
```

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```
210.0   0.160647E+02   0.432099E+01   0.453012E+01   0.249159E+02
220.0   0.161135E+02   0.490937E+01   0.469486E+01   0.257177E+02
230.0   0.161562E+02   0.552535E+01   0.486431E+01   0.265458E+02
240.0   0.161938E+02   0.616728E+01   0.503873E+01   0.273998E+02
250.0   0.162272E+02   0.683343E+01   0.521803E+01   0.282786E+02
260.0   0.162569E+02   0.752199E+01   0.540191E+01   0.291808E+02
270.0   0.162834E+02   0.823109E+01   0.558984E+01   0.301043E+02
280.0   0.163072E+02   0.895872E+01   0.578122E+01   0.310471E+02
290.0   0.163286E+02   0.970284E+01   0.597534E+01   0.320068E+02
300.0   0.163480E+02   0.104613E+02   0.617148E+01   0.329808E+02
310.0   0.163656E+02   0.112321E+02   0.636891E+01   0.339666E+02
320.0   0.163815E+02   0.120131E+02   0.656692E+01   0.349615E+02
330.0   0.163961E+02   0.128021E+02   0.676485E+01   0.359630E+02
340.0   0.164094E+02   0.135972E+02   0.696208E+01   0.369687E+02
350.0   0.164216E+02   0.143965E+02   0.715803E+01   0.379761E+02
360.0   0.164329E+02   0.151981E+02   0.735220E+01   0.389831E+02
370.0   0.164432E+02   0.160003E+02   0.754414E+01   0.399876E+02
380.0   0.164527E+02   0.168015E+02   0.773346E+01   0.409876E+02
390.0   0.164616E+02   0.176001E+02   0.791982E+01   0.419815E+02
400.0   0.164697E+02   0.183949E+02   0.810294E+01   0.429676E+02
410.0   0.164773E+02   0.191845E+02   0.828258E+01   0.439444E+02
420.0   0.164844E+02   0.199679E+02   0.845855E+01   0.449109E+02
430.0   0.164910E+02   0.207441E+02   0.863071E+01   0.458658E+02
440.0   0.164971E+02   0.215121E+02   0.879893E+01   0.468082E+02
450.0   0.165029E+02   0.222712E+02   0.896314E+01   0.477372E+02
460.0   0.165082E+02   0.230208E+02   0.912327E+01   0.486523E+02
470.0   0.165133E+02   0.237602E+02   0.927931E+01   0.495528E+02
480.0   0.165180E+02   0.244889E+02   0.943124E+01   0.504382E+02
490.0   0.165225E+02   0.252067E+02   0.957909E+01   0.513082E+02
500.0   0.165266E+02   0.259130E+02   0.972286E+01   0.521625E+02
510.0   0.165306E+02   0.266078E+02   0.986262E+01   0.530010E+02
520.0   0.165343E+02   0.272907E+02   0.999840E+01   0.538234E+02
530.0   0.165378E+02   0.279616E+02   0.101303E+02   0.546297E+02
540.0   0.165411E+02   0.286205E+02   0.102583E+02   0.554200E+02
550.0   0.165443E+02   0.292673E+02   0.103826E+02   0.561942E+02

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Zusammenfassung — Es wird ein automatisiertes Komputerprogram zur Berechnung der Wärmekapazität von Makromolekülen aus den durch die Tarasov-Gleichung beschriebenen Gerüstschwingungsfrequenzen und Gruppenschwingungsfrequenzen angegeben. Die für Polyäthylen und Polytetrafluoräthylen berechneten Wärmekapazitäten stimmen gut mit den experimentellen Daten unserer ATHAS-Datenbank überein. Das Programm wird einen Teil des geplanten ATHAS Computation Center bilden.

Резюме — Представлена автоматизированная машинная программа для вычисления теплоемкости макромолекул на основе скелетных колебательных частот, описанных уравнением Тарасова, и групповых частот колебаний. Вычисленные теплоемкости для кристаллических полиэтилена и политетрафторэтилена хорошо согласуются с экспериментальными данными из банка данных АТХАС. Эта программа будет частью запланированного АТХАС вычислительного центра.