Contribution of the Torsional Modes to the Equilibrium Distribution of Vibrational States and to the Specific Heat of a Chain Molecule *

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The torsional modes of a chain molecule were studied recently under the assumption that it has a well defined spatial configuration at any time. Here we show how the averages over the possible configurations, for a distribution in thermal equilibrium, should be performed in the calculation of the thermodynamical properties. Our results show that the mean density of torsional states increases in the low frequency region with increasing temperature. The specific heat behaviour shows a considerable difference from the result obtained in the previous paper, where only the lowest energetic configuration was considered. The consequences of this result with respect to the configurational properties of polymer molecules near the θ temperature are discussed.

I. Introduction

In a recent publication [1], two of us (C.S. and J.N.) have obtained a system of equations of motion for the degrees of freedom of the standard model [2] of a polymer molecule, consisting of a chain of N masses (monomers). The fundamental assumption was that at any given time the molecule can be described as being in an oscillatory state, with the angular coordinates of the bonds oscillating around a well defined configuration, characterized by a set of minima of the potential energy. In the case of molecules in solution, frequent jumps occur from one configuration to another [3]. The above assumption corresponds then to saying that if ω_0 is a typical oscillation frequency and τ_R a typical relaxation time between configurations, then $\omega_0 \tau_R \gg 1$. This is indeed the case for most of the situations of interest [4]. For a polymer solution in thermal equilibrium, the molecules are distributed in an enormous variety of distinct configurations, and the outcome of any measurement is the result of an average over all configurations. The purpose of this paper is to show how to perform this average in order to obtain the quantities of interest.

We make the present paper self-contained by repeating briefly the essential points of [1]. As we will see below, the equations of motion are written in terms of a configuration dependent "mass tensor", from whose eigenvalues one obtains the normal frequencies. A "density of states" is then defined for this configuration as the number of normal frequencies in a small interval $\Delta\omega$, divided by $\Delta\omega$. In [1] this was calculated explicitly for a very special configuration with all bonds in the trans conformation ($\varphi = 0°$). In the more realistic case of molecules in thermal equilibrium, the canonical average over configurations of the density of states, to be introduced below, is a more important quantity. The plan of the paper is the following: in Sect. II we derive the equations of motion and obtain the normal frequencies for an arbitrary configuration. In Sect. III we introduce the procedure for averaging over a canonical distribution of configurations. This method is applied in Sect. IV to calculate the contribution of the normal modes to the specific heat. In Sect. V we introduce the average density of states, studying its temperature dependence and the consequences of this dependence on the form of the specific heat. In addition we discuss the present

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method in comparison with the usual path integral approach to the problem.

II. Equations of Motion and Normal Frequencies

Here we give only the essential aspects of the model, and of the derivation of the equations of motion, refering the reader who asks for more details to Sects. II and III of [1]. The model molecule consists of a chain of N masses (monomers) separated from each other by a distance d, which will be taken as constant throughout this work. The instantaneous configuration of the molecule is then completely defined by giving the bond angles θ_j and the torsional angles φ_j. There is one common potential minimum for the bond angles, $\theta_j = \theta_0$ ($\approx 68°$ for polyethylene), and three different minima for the torsional angles, $\varphi_j = \alpha_j$, with $\alpha_j = 0°$ (trans conformation) or $\alpha_j = \pm 2\pi/3$ (gauche conformations). For mathematical convenience we imagine the molecule with one end bounded to a fixed coordinate system in such a way that we can associate also with the first two monomers the same potential well as for the others, namely,

$$U_j = \tfrac{1}{2} k_\theta (\theta_j - \theta_0)^2 + \tfrac{1}{2} k_\varphi (\varphi_j - \alpha_j)^2 + C_{\alpha_j}, \quad (1)$$

where $C_{\alpha_j} = 0$ or Δ if the j^{th} bond is in the trans or gauche conformation, respectively. In addition we have made a harmonic oscillator approximation for the local potential energy.

In order to simplify notations we introduce the generalized coordinates q_j, appropriate for angular oscillations around an equilibrium configuration $\alpha \equiv (\alpha_1, \ldots, \alpha_N)$, defined by

$$q_j = \varphi_j - \alpha_j, \quad j = 1, \ldots, N, \text{ torsional modes}, \quad (2\text{a})$$

$$q_{N+j} = \theta_j - \theta_0, \quad j = 1, \ldots, N, \text{ bond bending modes}. \quad (2\text{b})$$

The total potential energy will then be written as

$$U = \sum_{j=1}^{2N} k_j q_j^2 + \sum_{j=1}^{N} C_{\alpha_j}, \quad (3)$$

where $k_j = k_\varphi$ or k_θ for $j \leqq N$ or $j > N$, respectively.

To obtain the kinetic energy, $K = m \sum \dot{\boldsymbol{r}}_j^2/2$, in terms of $\dot{q}_j$ we use the transformation matrices introduced by Flory [2], who shows that the Cartesian coordinates of two consecutive masses along the chain are related by $\boldsymbol{r}_j = \boldsymbol{r}_{j-1} + \tau_j \boldsymbol{\varrho}$, where

$$\boldsymbol{r}_j \equiv \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix}, \quad \boldsymbol{\varrho} = \begin{pmatrix} d \\ 0 \\ 0 \end{pmatrix}, \quad (4)$$

$$\tau_j = T_1 T_2 \ldots T_j \quad (5)$$

and

$$T_i = \begin{pmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\varphi_i & -\cos\theta_i \cos\varphi_i & \sin\varphi_i \\ \sin\theta_i \sin\varphi_i & -\cos\theta_i \sin\varphi_i & -\cos\varphi_i \end{pmatrix}. \quad (6)$$

A straightforward calculation leads to the following expression for the kinetic energy of vibration around a given equilibrium configuration α,

$$K = \frac{1}{2} \sum_{i,l=1}^{2N} M_{il} \dot{q}_i \dot{q}_l, \quad (7)$$

where

$$M_{il} = m d^2 \sum_{j,k=1}^{2N} \sum_{\mu=1}^{3} (\tau_j^{(i)})_{\mu 1} (\tau_k^{(l)})_{\mu 1} [N+1-\mathrm{Max}(j,k)] \quad (8)$$

and

$$\tau_j^{(i)} \equiv \partial \tau_j / \partial q_i .$$

The "mass tensor" M_{il} depends not only on α but also on all coordinates $q_1 \ldots q_{2N}$. When we substitute the Lagrangian $L = K - U$ into the Euler-Lagrange equations we obtain equations of motion with terms containing the derivatives of M. Since these terms contain at least one factor of q_j more than the others and since we consider only small amplitude oscillations ($q_j \ll 1$), they will be neglected in the following. Thus we are left with the following system of equations of motion

$$\sum_{l=1}^{2N} M_{il} \ddot{q}_l + k_i q_i = 0, \quad i = 1, \ldots, 2N. \quad (9)$$

where the M_{il} are calculated at the equilibrium angles, $\varphi_j = \alpha_j$ and $\theta_j = \theta_0$.

The system of Eqs. (9) will have non-trivial solutions (normal modes) with frequencies ω_k, $k = 1, \ldots, 2N$, if

$$\mathrm{Det}\,(W_{il} - \lambda_k \delta_{il}) = 0, \quad (10)$$

where

$$W_{il} \equiv M_{il}/k_i, \quad \lambda_k = 1/\omega_k^2, \quad (11)$$

i.e., the normal frequencies ω_k are obtained from the eigenvalues of the (modified) mass tensor.

III. Thermal Averages

Since each bond may be found in any of 3 different conformations, the total number of configurations of the molecule is $3N$. Thus, even for a rather small molecule (we take $N = 40$ in the numerical calculations presented below) an exact calculation of averages, where the contribution of every possible configuration is explicitly taken into account, is completely impractical. An obvious approximation procedure is to choose randomly a number of configurations, with the appropriate probability distribution, and then taking the arithmetic average of the results obtained for each configuration. However, since the Boltzmann distribution is temperature dependent, for each temperature value a new sample of configurations has to be selected and the corresponding mass tensors diagonalized. This method turns out to be exceedingly time consuming and, since it is impossible to use a very big sample, the results show very large fluctuations, depending on the sample choice. In the following we present an alternative statistical method which is much less time consuming and much less dependent on the random choice of this sample.

A quantum mechanical state of a given configuration with n gauches has energy

$$E = \sum_{k=1}^{2N} \hbar\,\omega_k \left(n_k + \frac{1}{2} \right) + n\Delta\,. \tag{12}$$

The numbers n_k, which we call "number of phonons in mode k", obey Bose-Einstein statistics, with expectation value

$$\bar{n}_k = \frac{1}{\exp\{\beta\,\hbar\,\omega_k\} - 1}\,. \tag{13}$$

We define the configurational energy E_α as that part of (12) which is independent of the number of phonons, i.e.,

$$E_\alpha = \sum_{k=1}^{2N} \frac{1}{2}\hbar\,\omega_k + n\Delta \tag{14}$$

and the phonon energy as

$$E_\mathrm{p} = \sum_{k=1}^{2N} \hbar\,\omega_k\, n_k\,. \tag{15}$$

The inclusion of the zero-point energy in E_α is necessary because, being configuration dependent, it has to be included in the Boltzmann distribution for the configurations. The probability that a configuration α occurs is

$$P_\alpha = z_\alpha\, e^{-\beta E_\alpha} / \sum_{\alpha'} z_{\alpha'}\, e^{-\beta E_{\alpha'}}\,, \tag{16a}$$

where

$$z_{\alpha'} = \prod_{k=1}^{2N} \left(1 - \exp(-\hbar\,\omega_k(\alpha')\,\beta)\right)^{-1}.$$

Because the probability of a configuration is mainly determined by the energies E_α at low temperatures we will set $z_\alpha = z_{\alpha'} = 1$ in the following and use

$$P_\alpha = e^{-\beta E_\alpha} / \sum_{\alpha'} e^{-\beta E_{\alpha'}}\,. \tag{16b}$$

A configuration α is characterized by n, the number of gauches and by the precise kinds and positions of the gauches, which we represent generically by m, i.e., $\alpha \equiv (n; m)$. Thus (16b) may be written more explicitly as

$$P_\alpha = \frac{\exp\{-\beta n\,\Delta\}\,\exp\{-\beta \frac{1}{2} \sum \hbar\,\omega_k(n; m)\}}{\sum\limits_{n'} \exp\{-\beta n'\Delta\} \sum\limits_{m'} \exp\{-\beta \frac{1}{2} \sum \hbar\,\omega_k(n'; m')\}}\,. \tag{17}$$

Our numerical calculations show that the sums appearing in the exponents in (17), $\sum \hbar\,\omega_k\,(n; m)$, are strongly dependent on n, the number of gauches but only slightly dependent on their precise types and positions, m. For a random choice of configurations with a given n, the said sums are distributed in a narrow band around the average value

$$S_n = \langle \sum_k \hbar\,\omega_k\,(n; m) \rangle_m\,. \tag{18}$$

Accordingly, we will substitute (17) by the approximate expression

$$P_\alpha \equiv P_{(n;m)} \simeq \frac{\exp\{-\beta\,(n\Delta + S_n/2)\}}{\sum\limits_{n'm'} \exp\{-\beta\,(n'\Delta + S_{n'}/2)\}}\,. \tag{19}$$

For a given n there exist

$$\chi_n = 2^n\, C_N^n = \frac{2^n N!}{(N-n)!\, n!} \tag{20}$$

distinct configurations. Thus, the probability that a molecule is in a configuration with n gauches is

$$P_n = \chi_n\, P_{(n;m)} = \frac{\chi_n \exp\{-\beta\,(n\Delta + S_n/2)\}}{\sum\limits_{n'} \chi_{n'} \exp\{-\beta\,(n'\Delta + S_{n'}/2)\}}\,. \tag{21}$$

In Fig. 1 we show the numerical results for S_n obtained with a sample of 10 configurations for

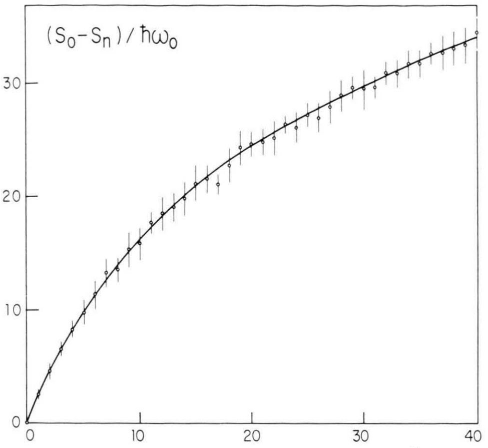

Fig. 1. S_0-S_n in units of $\hbar\,\omega_0$ as function of the number n of gauches, where $S_0=\sum \hbar\,\omega_k$ for the pure trans configuration. For details, see text.

each n, and with $N=40$, in the limit $k_\theta=\infty$. As energy unit we use $\hbar\,\omega_0$, where

$$\omega_0=\frac{k_\varphi}{m\,d^2\sin^2\theta_0} \tag{22}$$

is the frequency of the single particle oscillator associated with the torsional potential well $U=\frac{1}{2}\,k_\varphi\,\varphi^2$. For polyethylene this frequency is estimated to be $\approx 10^{13}$/s. Taking $k_\theta=\infty$ (in polyethylene $k_\theta \gg k_\Phi$) is equivalent to fixing $\theta=\theta_0=$ constant, as was done in the numerical calculations of [1]. As a consequence we then have N, and not $2N$ modes and the mass tensors to be diagonalized are of order N. For a comparison of the theory with experiment it may turn out necessary to include also the θ-vibrations. For our present purpose of analyzing the qualitative aspects of the results, however, this simplified calculation is sufficient. The limitation to N modes is made in all numerical studies presented in this paper, although the theory is not restricted to this case. If the even more energetic vibrations, those of the bond length d, should be included, then some revision of the original theory would be required. In Fig. 1 the dots represent S_n for the randomly selected sample, the vertical lines represent the bandwidth within which the values of $\sum \hbar\,\omega_k$ for the different configurations of the sample are located. The continuous line is a hand-drawn "smoothing", which we believe to represent better the values of S_n in the limit of large samples. In what follows we use for S_n this smoothed value.

IV. Specific Heat

In Sect. III we divided the energy of a molecular state in two parts,

$$E=E_\alpha+E_{\mathrm{p}}, \tag{23}$$

where the configuration energy E_α and the phonon energy E_{p} are given by (14) and (15). We define, accordingly, two specific heats,

$$C_{\mathrm{c}}=\frac{\partial}{\partial T}\langle E_\alpha\rangle_\alpha \tag{24}$$

and

$$C_{\mathrm{p}}=\frac{\partial}{\partial T}\langle \bar{E}_{\mathrm{p}}\rangle_\alpha, \tag{25}$$

where $\langle\ldots\rangle_\alpha$ represents the average over configurations and $\bar{E}_{\mathrm{p}}$ means that in (15) the number of phonons is substituted by its expectation value $\bar{n}_k$, given by (12). Following the procedure outlined in Sect. III, one obtains

$$\langle E_\alpha\rangle_\alpha=\sum_n P_n\,E_{\mathrm{c}n} \tag{26}$$

and

$$\langle \bar{E}_{\mathrm{p}}\rangle_\alpha=\sum_n P_n\,E_{\mathrm{p}n}, \tag{27}$$

where

$$E_{\mathrm{c}n}=n\Delta+S_n/2 \tag{28}$$

and

$$E_{\mathrm{p}n}=\frac{1}{\chi_n}\sum_m \bar{E}_{\mathrm{p}}=\frac{1}{\chi_n}\sum_m\sum_k \hbar\,\omega_k\,\bar{n}_k \tag{29}$$

are the average configuration energy and the average phonon energy for the configurations with n gauches. This "partial average" is performed numerically by randomly selecting χ configurations, obtaining the corresponding ω_k's for each of them, and then taking the arithmetic average over the values obtained for $\bar{E}_{\mathrm{p}}$.

A straightforward calculation gives, for the configurational specific heat, the expression

$$C_{\mathrm{c}}=\frac{1}{k_{\mathrm{B}}T^2}\left[\langle E_{\mathrm{c}n}^2\rangle_n-\langle E_{\mathrm{c}n}\rangle_n^2\right], \tag{30}$$

where $\langle\ldots\rangle_n$ means $\sum P_n\ldots$, i.e., average over all possible number of gauches. It is interesting to note that C_{c} is proportional to the variance of the configuration energy. For the phonon specific heat one obtains

$$C_{\mathrm{p}}=\left\langle\frac{\partial E_{\mathrm{p}n}}{\partial T}\right\rangle_n+\frac{1}{k_{\mathrm{B}}T^2}\left[\langle E_{\mathrm{c}n}E_{\mathrm{p}n}\rangle_n-\langle E_{\mathrm{c}n}\rangle_n\langle E_{\mathrm{p}n}\rangle_n\right]. \tag{31}$$

The first term above is the most important one. It is the only one which occurs when, as in [1], the trans configuration is considered exclusively. The temperature derivative occurring in (31) may easily be obtained from (29) and (13),

$$\frac{\partial E_{pn}}{\partial T} = \frac{1}{k_B T^2} \frac{1}{\chi_n} \sum_m \sum_k \hbar^2 \omega_k^2 \bar{n}_k (\bar{n}_k + 1)\,. \quad (32)$$

The second term of (31) is a correction proportional to the correlation between the configurational and phonon energies, whose origin will be made clearer in the next section.

Our numerical calculations were done for a chain of $N = 40$ monomers. We have randomly selected $\chi = 10$ configurations for each number $n = 1$ to 40 of gauches. For the physical parameters we have chosen the values appropriate to polyethylene, namely [2] $\theta_0 = 68°$, Δ / k_B between 200 K and 300 K and $\omega_0 \approx 10^{13}$/s. The important parameter for our calculations is the ratio $\hbar \omega_0 / \Delta$, which can be estimated to lie somewhere between 0.2 and 0.5. In Fig. 2 we show the configurational specific heat C_c, obtained from (30) for some values in this range. In the limit $\hbar \omega_0 / \Delta \to 0$ the contribution of S_n to C_c vanishes, and we recover the result obtained in [1], which is also shown in Fig. 2 for comparison. We can see that for the realistic values of the parameters the contribution of the zero point energy is not negligible.

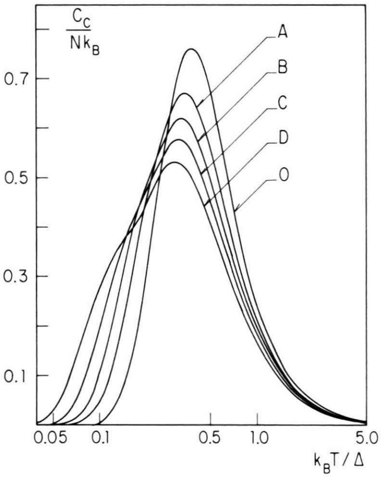

Fig. 2. Configurational specific heat per bond versus temperature, for several values of the parameter $\hbar \omega_0 / \Delta$, namely 0.2, 0.3, 0.4 and 0.5 for curves A, B, C and D respectively. Curve O is the extreme case studied in [1], where S_n is neglected in the Boltzmann factor, which is correct in the limit $\hbar \omega_0 / \Delta = 0$.

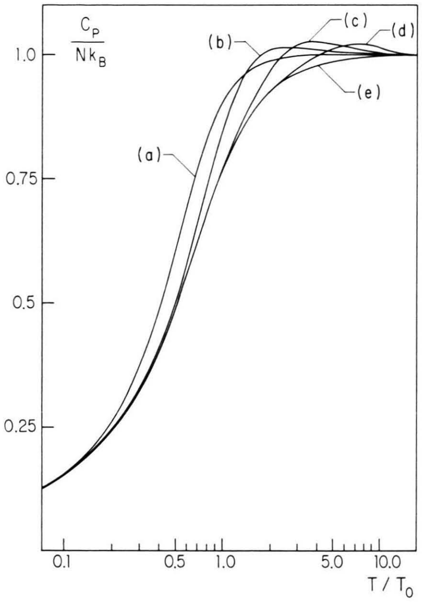

Fig. 3. Phonon specific heat per bond versus temperature in units of $T_0 = \hbar \omega_0 / k_B$, for several values of the parameter $\Delta / \hbar \omega_0$, namely 2.5, 5.0, 10.0 and 20.0 for curves a, b, c and d. Curve e applies to the pure trans configuration, studied in [1], which corresponds to the limit $\Delta \to \infty$.

In Fig. 3 the phonon specific heat C_p, obtained from (31), is shown. Here the natural unit of temperature is $T_0 = \hbar \omega_0 / k_B$ and the curves correspond to different values of the ratio $\Delta / \hbar \omega_0$. Some very large values of Δ have been included to show how the curves tend to the limit $\Delta \to \infty$, which corresponds to the pure trans configuration, calculated in [1]. In Fig. 4 we have plotted separately the first term of (31) and the correlation dependent correction. Finally, we show in Fig. 5 the total specific heat $C_c + C_p$, for various values of $\hbar \omega_0 / \Delta$, using again Δ / k_B as unit of temperature.

V. Average Density of States and Discussion

In [1] the density of states $\varrho(\omega)$ was defined for a given configuration. From the numerical results for the pure trans configuration one sees that, for not too small N, the density of states per bond $\varrho(\omega)/N$ is virtually independent of N. This observation allows us to work with moderate values of N and to extrapolate the results to the case of very long chains. Now we are considering an ensemble of molecules in thermal equilibrium. Thus, what we need in order to calculate thermodynamical quanti-

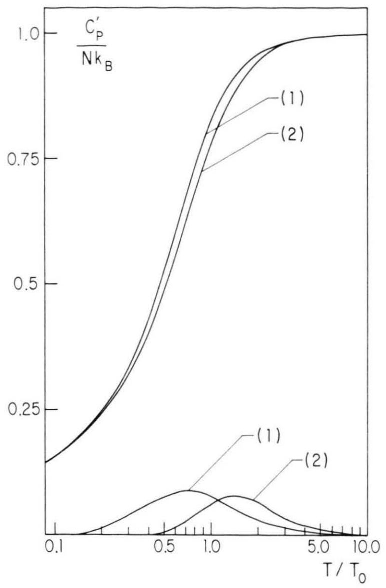

Fig. 4. The contribution of the two terms of (31) for the phonon specific heat. Curves (1) correspond to $\Delta/\hbar\,\omega_0 = 2.5$ and curves (2) to $\Delta/\hbar\,\omega_0 = 5.0$. The top curves represent the first term of (31) and the lower ones the second, or correlation corrections.

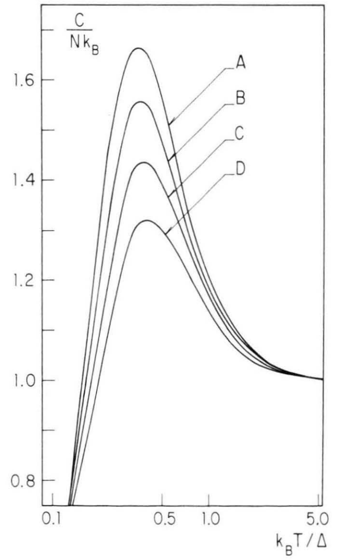

Fig. 5. Total specific heat per bond for several values of the parameter $\hbar\,\omega_0/\Delta$, namely 0.2, 0.3, 0.4 and 0.5 for curves A, B, C and D, respectively.

ties, is a density of states $\bar{\varrho}(\omega)$, averaged over all possible configurations, with probability distribution given by (21). This has been obtained for the sample described in the previous section. Using $\chi = 10$ distinct configurations for any number n of gauches and $N = 40$ normal modes per configuration, we obtain 400 normal frequencies for each n (except for $n = 0$, since the pure trans configuration is unique, giving only N frequencies). Next we count the number of frequencies in the arbitrary (but small) interval $\Delta\omega$, around ω, divide the result by the number χ of configurations and by $\Delta\omega$, multiply by P_n given by (21) and sum over all values of n. Since P_n is temperature dependent, the last two steps have to be repeated for all temperatures of interest. With this procedure we obtain the dots shown on the graphs of Figure 6. The continuous lines are hand drawn smoothings, which we believe to approximate better the density of states of a very long chain, and/or bigger samples, for which the "noise", dependent on our arbitrary choice of the intervals $\Delta\omega$, is automatically smoothed out due to the presence of a much bigger number of normal frequencies.

All graphs of Fig. 6 are done for $\Delta/\hbar\,\omega_0 = 2.5$. It is interesting to note how the form of $\bar{\varrho}(\omega)$ changes with temperature: For larger T the center of gravity of the curves shifts to the left, increasing the density of states at lower frequencies. This fact allows us to understand the behaviour of the phonon specific heat obtained in the previous section. The average value of the phonon energy, as given by (27) and

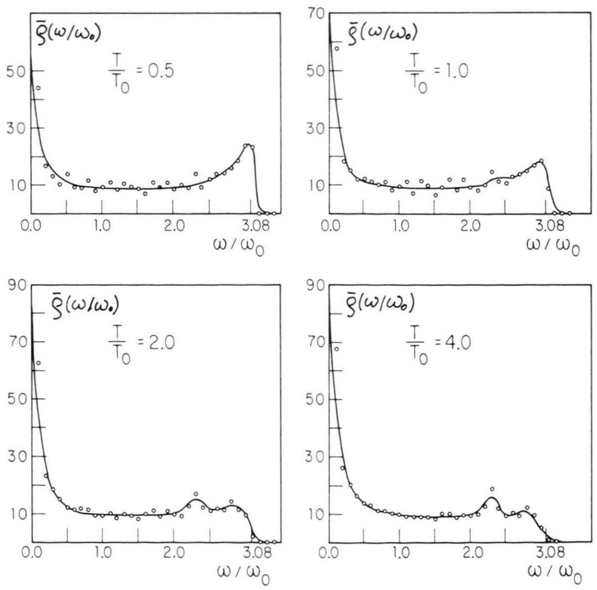

Fig. 6. Average density of states $\bar{\varrho}(\omega)$ for the case $\Delta/\hbar\,\omega_0 = 2.5$, for several values of the reduced temperature T/T_0, where $T_0 = \hbar\,\omega_0/k_B$. For details, see text.

(29), may be written as

$$\langle \bar{E}_{\mathrm{p}} \rangle_{\alpha} = \int \mathrm{d}\omega\, \bar{\varrho}(\omega)\, \hbar\, \omega\, \bar{n}(\omega) \tag{33}$$

with $\bar{n}(\omega)$ given by (13). The product $\omega\, \bar{n}(\omega)$ is a monotonically decreasing function of ω, for fixed temperature and a monotonically increasing function of temperature for fixed ω. Thus, although for a fixed configuration (i.e., $\bar{\varrho}(\omega)$ independent of T), the average phonon energy increases with T only because $\bar{n}(\omega)$ increases, allowing an equilibrium distribution for the configurations the integral of the product $\omega\, \bar{n}(\omega)\, \bar{\varrho}(\omega)$ will increase even more rapidly because $\bar{\varrho}(\omega)$ will shift towards the region of small ω, where $\omega\, \bar{\varrho}(\omega)$ is bigger. This effect is more pronounced for smaller values of Δ and vanishes in the limit $\Delta \to \infty$, for which only the trans configuration is allowed, in agreement with the numerical results shown in Figure 3.

By differentiating (33) with respect to the temperature, one obtains the phonon specific heat in terms of $\bar{\varrho}(\omega)$,

$$C_{\mathrm{p}} = \int \mathrm{d}\omega\, \hbar\, \omega \left[\bar{\varrho}(\omega)\, \frac{\partial \bar{n}(\omega)}{\partial T} + \bar{n}(\omega)\, \frac{\partial \bar{\varrho}(\omega)}{\partial T} \right]. \tag{34}$$

It is clear that the first and second terms of the integrand correspond, respectively, to the first and second terms of (31). One sees now that the correlation term of (31) comes from the variation of $\bar{\varrho}(\omega)$ with temperature.

As a conclusion, based on our numerical results, we can say that the introduction of an equilibrium distribution of configurations produces a non negligible change of the specific heat as well as of the density of states, in comparison with the results obtained in [1] for the pure trans configuration. A next step in improving the theory consists in taking into account the interaction of the molecule with the solvent, a problem which is presently under study.

Eventually we would like to make some comparative remarks with respect to the problem of steric contraints in connection with the path integral formalism usually applied to macromolecules [5]. The set of configurations $\{[n; m]\}$ has been defined below (16b). However, not all such configurations may be realizable in real space due to the self avoiding walk constraints on the polymer molecule's configurations leading to the excluded volume effect. In addition those configurations $\{[n; m]'\}$ which are realizable may require additional interaction terms in (1) due to self contact on account of finite amplitude oscillations. Obviously therefore the present approximation corresponds to a random walk of fixed step length d and random but sharp torsional angles $\alpha_j = 0, \pm 2\pi/3$, because the coordinate dependence of the mass tensor M_{il} is neglected as pointed out below (8). However, due to the zero-point energy dependence of the configurational probability $P_{\alpha'}$, a long range interaction is established along the polymer molecule. This leads to non-Markovian properties of the random walk. In the present approximation, where the band width of the quantities leading to the average S_n is neglected the memory just stores n, the number of gauches.

The next better approximation to use would be to take the mass tensor M_{il} to be dependent on the $2N(2N+2)/2$ correlation functions $\langle q_n K_{nm}(\alpha)\, q_m \rangle$, evaluated for fixed configuration α and T. Here $K_{nm}(\alpha)$ is obtained from (8). Because with increasing N small amplitude and slow fluctuations at one bond lead to large amplitude and fast fluctuations in the coordinates of distant bonds (measured along the molecule) large amplification will occur for some modes. It is obvious therefore, that self contact in the present model is essentially dynamically generated and for very large N, i.e., $N \gg 40$ must be taken into account at all T, via additional terms to (1). However, now the problem is that for a given $[n; m]$ many possible additional equilibrium states exist (except for $n/N \ll 1$) which are reached physically through slow wormlike motion of the polymer molecule. For each such state severe nonlinear constraints must be imposed on the phonon problem (e.g. joint motion of entanglement points) in order not to overcount the degrees of freedom of the system. As a matter of fact within the present treatment of the problem the whole phase space belonging to these additional equilibrium states for a given $[n; m]$ is covered by the harmonically excited phonons from the respective groundstate represented by $[n; m]$ itself. It follows from this that the present approximation is useful, over the whole temperature range, only for small N or paraffin molecules, whereas for large N and in the high temperature limit it corresponds approximately to the free random walk approximation in polymer physics. The low temperature regime, however, is treated in a more accurate fashion by the present method. An improved version of the present treatment with the purpose to take the topological constraints into account consists in modifying (20) by means of a pseudopotential depending on $[n; m]$. This then leads to a more complex memory effect and in the high temperature limit the procedure may be equivalent to the one used in the path integral formalism.

The interesting result of the present study is that the specific heat of the phonon system is configuration dependent as implied by the second term of (31) or (34). From this follows that with increasing T the approximation leading from (16a) to (16b) may break down, and taking $z_\chi \neq z_{\chi'}$ into account may lead to an amplification of this effect. In the latter case the non-Markovian property of the probability distribution P_χ is amplified with increasing T and therefore the long range interactions along the polymer molecule as mediated by the phonons may lead to observable effects. In case such effects also survive in the presence of a solvent then this may have interesting consequences for the configurational properties of the polymer molecule at the θ temperature. Because at that temperature the static properties of the polymer molecule are just independent of the topological constraints ignored in the present study, the phonon effects on the configurational distribution as predicted above may become important. Studies to determine the configurational observables of a polymer molecule within the present theory are in progress.

In conclusion the authors acknowledge stimulating suggestions by F. Rys.

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