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## Abstract

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# On the Theory of the Heat Capacity of Linear Polymers at Low Temperatures

## Vibrational Spectrum and Heat Capacity

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Experimental data on investigations of the heat capacity of linear polymers at low temperatures (1–6) indicate the existence, over a considerable temperature interval (∼ 100°), of an essentially linear dependence of heat capacity on temperature.

The continuum model proposed by V. V. Tarasov (7) for considering the heat capacity of chain structures appears to us theoretically unjustified, since in it only valence forces are in fact taken into account, whereas for a real polymer chain in the temperature interval under consideration the principal role is played by skeletal torsional and deformation vibrations (8). The continuum model considered by I. M. Lifshits (9) is physically better justified, since it takes into account the bending stiffness of chains. However, the use of this model does not make it possible to consider the individual features of particular polymers. The crudeness of the molecular model considered by Stockmayer and Hecht (10) and by Genensky and Newell (11) does not permit comparison of calculated data with experimental data.

In the present work the heat capacity of the simplest linear polymers—polyethylene and polytetrafluoroethylene—has been calculated using values of force constants obtained from infrared vibrational spectra (12–14). In the calculation it was assumed that the carbon skeleton for both polymers forms a regular planar zigzag. For crystalline polyethylene this is consistent with known X-ray structural data. Crystalline polytetrafluoroethylene is a slightly twisted helix (13 monomers per turn). Real polymers are not completely ordered formations. However, comparison of the experimental heat-capacity values for amorphous and crystalline polyisobutylene shows that the heat capacity is very weakly sensitive to changes in the degree of crystallinity (15). The results of calculations of the infrared spectra of polyethylene and Teflon, carried out on an analogous planar model, are in satisfactory agreement with experimental data (12,16,17).

Polymers are strongly anisotropic structures. The force constants corresponding to interchain interaction are much smaller than the force constants for in-

Fig. 1. Dispersion relation

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Fig. 2. Distribution function

Figure 2: Fig. 2. Distribution function

trachain valence and deformation vibrations. In our calculation the influence of intermolecular interaction on the vibrational spectrum and heat capacity of polymer chains is not taken into account. As estimates in ($^{11}$) show, there exists a region of low temperatures in which intermolecular interaction may be neglected. The difficulties of calculation for a three-dimensional model of a real polymer do not yet allow us to determine the theoretical boundaries of the temperature interval in which the influence of intermolecular interaction on the heat capacity is insignificant. Comparison of the results of calculations given below⋯

taking account of the experimental data indicates that in the temperature range from 50° K and higher for Teflon and from 90° K for polyethylene, good agreement with experiment is obtained even without taking into account the effect of intermolecular interaction on the frequency distribution function.

The calculation of the vibrational spectrum of a long regular polymer chain, regarded as a one-dimensional crystal with a complex cell, was carried out on the basis of the Born—Karman method.

For polyethylene, nonplanar skeletal torsional vibrations—type A, planar skeletal deformation vibrations—type B, and external deformation— “pendulum” —vibrations of $CH_2$ groups—type C—were considered. An estimate of the contribution to the heat capacity from the other branches of the vibrational spectrum shows that the role of these vibrations in the temperature range investigated is negligibly small.

### Fig. 1. Dispersion relation

In calculating vibrations for branches of types A and B, the $CH_2$ groups were assumed to be point masses with the mass concentrated at the carbon atom. The force constant $K = 0.02 \cdot 10^5$ dyn/cm for frequencies of type A was taken from $^{(14)}$. The dispersion relation $\nu(\theta)$ and the frequency-spectrum density $G(\nu) \sim d\theta/d\nu$ for branch A are shown in Fig. 1 ($\theta$ is the phase shift between vibrations of neighboring cells). Near the frequencies corresponding to the values $\theta_1 = 0$ and $\theta_2 = 109.71°$, $G(\nu)$ has singularities of the form $G(\nu) \sim 1/\sqrt{\nu}$ as $\nu \to 0$ and $G(\nu) \sim 1/\sqrt{\nu(\theta_2) - \nu}$ as $\nu \to \nu(\theta_2)$, characteristic of a one-dimensional vibrational spectrum $^{(22)}$. For calculating vibrations of branch B the force constants were taken from $^{(13)}$. The peculiarities in the behavior of the dispersion relation $\nu(\theta)$ and the frequency dependence $G(\nu)$ are of the same type as in case A.

**Fig. 2. Distribution function**

The heat capacity was calculated by numerical integration with the distribution function

$$c = \sum_{l=1}^{m} \int_{\nu_{l\,\min}}^{\nu_{l\,\max}} \frac{(h\nu/kT)^2 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2} G_l(\nu)\, d\nu, \tag{1}$$

where $\nu_{l\,\min}$ and $\nu_{l\,\max}$ are the minimum and maximum frequency values in the $l$-th branch, and $m$ is the number of branches.

Direct integration of (1) with the function $G_l(\nu) \sim d\theta(\nu)/d\nu$ is practically difficult; therefore the functions $G(\nu)$ were represented as a sum of a polynomial and singular terms of the form $1/\sqrt{\nu}$ or $1/\sqrt{\nu_{\max} - \nu}$, approximating the behavior of the distribution function near singular points.

For calculating the branch of the vibrational spectrum corresponding to vibrations of type C, exact equations of motion for paraffin chains and force constants from work $^{(21)}$ were used. Calculations for branch C show that in the temperature interval from 90 to 180° K the contribution of pendulum vibrations to the heat capacity becomes appreciable ($\sim$ 3–5%) only at temperatures above 150° K. The results of calculating the vibrational heat capacity of polyethylene as a function of temperature are given in Fig. 2.

Similar calculations for the vibrational spectrum and heat capacity were carried out by us for a polytetrafluoroethylene chain. Since the mass of the fluorine atom is greater than the mass of the hydrogen atom, it proved necessary to take account of a larger number of vibrational branches. In addition to branches of types A, B, and C, consid-

in the case of polyethylene, a significant contribution to the heat capacity is made by torsional vibrations—type D, deformation "scissoring" vibrations—type E, as well as "wagging" vibrations—type F—of the $CF_2$ groups.

In considering the vibrational branch of type A, we assumed that the $CF_2$ groups move as a single whole, and took into account that the center of mass of a $CF_2$ group does not coincide with the carbon atom of the skeleton ($^{23}$). In the literature there are no data on the values of the force constant for nonplanar skeletal torsional vibrations of Teflon. Our variation of the values of this constant from the value previously adopted for polyethylene up to a value five times larger leads, in the temperature interval under consideration, to an insignificant change in the heat capacity for the branch of skeletal torsional vibrations.

**Fig. 3.** Comparison of calculated results (points) with experimental data (curves): 1—Teflon, 2—polyethylene

In studying branch B, we considered, pairwise, the influence of other types of vibrations of the same symmetry (valence skeletal vibrations, and "wagging" and "scissoring" vibrations of the $CF_2$ group) on the dispersion dependence $\nu(\theta)$. The

Figure 3: Comparison of calculated results (points) with experimental data (curves). 1—Teflon, 2—polyethylene

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calculations indicate the necessity of taking into account the coupling between deformation and valence skeletal vibrations; at the same time, it proves possible to neglect the influence of the other two types of vibrations. The dispersion dependences $\nu(\theta)$ and the density of the frequency spectrum $G(\nu)$ for branches A and B for Teflon are similar to the corresponding dependences for branches A and B in polyethylene.

In calculating the dispersion dependence and the distribution function in the case of branch D, its interaction with branch C was taken into account (the reverse influence is practically absent), and in calculating branch C the interaction with antisymmetric valence $CF_2$ vibrations was taken into account. (The contribution of the valence $CF_2$ vibration itself to the heat capacity in the frequency interval considered is absent.) Branches E and F, the highest-frequency of the types of vibrations considered, give a noticeable contribution to the heat capacity beginning at temperatures of $\sim 100°$K. In calculating them, interactions with all vibrations of the $CF_2$ group of the same symmetry were taken into account.

The density of the frequency spectrum for branches C, D, E, and F has singularities of the type

$$\frac{1}{\sqrt{\nu-\nu_{\text{min}}}} \quad \text{or} \quad \frac{1}{\sqrt{\nu_{\text{max}}-\nu}},$$

for frequencies corresponding to

$$\theta = 0 \quad \text{and} \quad \theta = \pi.$$

The heat capacity of polytetrafluoroethylene was calculated by the same method as for polyethylene. The results of the theoretical calculation and the experimental data ($^5$) are shown in Fig. 3.

Our calculations show that the vibrational heat capacity, computed on the basis of a set of force constants taken from spectroscopic data, is in good agreement with experiment over a wide temperature interval: 90–180°K for polyethylene and 50–200°K for Teflon. We note that the upper limit for polyethylene is determined by the glass-transition temperature; for Teflon, allowing for other, higher-frequency vibrational branches could probably shift the upper limit toward higher temperature values.

It follows from the calculations carried out that the practically linear dependence of heat capacity on temperature observed at low temperatures appears as a result of the superposition of the contributions, changing nonlinearly with temperature, from different branches of the entire low-frequency vibrational spectrum of the polymer chain.

For polyethylene, the contribution of skeletal vibrations is the determining one, whereas in the case of Teflon it amounts on average to about 40% of the total heat capacity. It may be expected that for most polymers with "heavy" side groups, such as polyvinylidene chloride, polytrifluoroethylene, etc., the share of the heat capacity due to deformational vibrations of the skeleton is no more than half of the total heat capacity, while the remaining part is determined by deformational vibrations of the side groups. We note that the contribution of valence skeletal vibrations is negligible even at room temperatures.

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*Note: Figure translations are in progress. See original paper for figures.*