

Vibrational spectral density in the long-wave range for a polymer chain with configurational disorder

M. Schulz and K. Handrich

Technische Hochschule 'Carl Schorlemmer' Leuna-Merseburg, Sektion Physik, Merseburg 4200, GDR

(Received 12 October 1988; revised 19 January 1989; accepted 31 January 1989)

The calculation of the configurational averaged vibrational spectrum $\langle G(\lambda) \rangle$ for a disordered polymer chain in the long-wavelength limit is presented. The possibility of constructing a simple continuous polymer chain model, which contains all necessary terms for the calculation of the potential energy, is considered. The configurational average of the spectral density is obtained by the replica method. To obtain analytical results, an expanded Hartree-Fock approximation is used; thereafter the configurational averaged spectral density is calculable by application of saddle-point integration. As a result of these calculations, a self-consistent equation is found, the solution of which gives $\langle G(\lambda) \rangle$.

(Keywords: spectral density; replica method; low-frequency range; saddle-point integration, configurational average)

INTRODUCTION

The calculation of harmonic motion in a polymer chain is a subject of great importance for several experiments. Especially for observations in inelastic neutron scattering, Raman scattering and infra-red absorption, it is necessary to know the vibrational density. The first calculations of vibrations along an all-*trans* chain were given by Kirkwood¹. Zbinden² used the same chain, but he took into consideration two different monomer units. In another work³ the authors calculate the vibrational spectrum of a chain with disordered distributions of the monomers in a copolymer. Halley⁴ gives a numerical simulation of a chain with stochastic structure, embedded in a self-avoiding walk on a diamond lattice.

The object of our calculations is the vibrational spectrum of a polymer chain with a disordered spatial structure. In this paper we will restrict ourselves exclusively to the long-wave range, which determines the thermodynamic properties at low temperature. Therefore it is acceptable that the influence of other components of motion (for example, relaxation modes) on the thermodynamic properties is small in comparison to the long-wave oscillations. This low-temperature region is of importance not only for spectroscopy but also for the calculation of the heat capacity at low temperatures. Note that in this case the T dependence of the heat capacity of polymers is determined by the vibrational spectrum in the low-frequency range, which corresponds to long-wave backbone vibrations.

MODEL

By restriction to the long-wave case it is possible to use a continuous model for the polymer chain. We first give a construction of the equation of motion of our chain model.

We can accept that a crossing between two different

chain configurations with respect to an oscillation period is very rare at low temperatures. Therefore it is reasonable to use a polymer chain with a static structure. The long-range interaction — for example, the excluded-volume effect — for a static chain has an important influence on the statistical weight for an individual configuration, but for the dynamics of the oscillations along the polymer chain we can neglect this effect. Note that for chain dynamics involving configurational crossing the application of this phantom chain is undoubtedly inappropriate. For this reason the model we choose is a chain of N monomer units of mass m_0 in which there are only interactions along the backbone. Assuming that for an individual monomer the deviation y_i of the topical position r_i from the equilibrium position r_i^0 (the coordinates of the static chain) is sufficiently small, we can work within the harmonic approximation.

We follow the ansatz of Helfand, Skolnick and others⁴⁻⁷. Here the potential energy is the sum of the squared differences of the deformed bond lengths $b_i = r_{i+1} - r_i$:

$$U_1 = \frac{1}{2} k_0 \sum_{i=1}^{n-1} (|b_i| - b_0)^2 \quad (1)$$

and the angles θ_i between neighbouring bond vectors:

$$U_2 = \frac{1}{2} w \sum_{i=1}^{n-2} (\cos \theta_i - \cos \theta_0)^2 \quad (2)$$

with reference to the equilibrium value of the bond length b_0 and of the bond angle θ_0 , respectively (k_0 and w are force constants). It can be easily seen that the terms of equation (2) are proportional to $(\theta_i - \theta_0)^2$ in the harmonic case.

All other contributions to the potential energy — for example, the energy for the rotational motion of the monomers — are neglected in this model.

Expressions (1) and (2) in the harmonic approximation are quadratic terms of $\delta y_i = y_{i+1} - y_i$. Assuming that

$\{b_i^0 = r_{i+1}^0 - r_i^0; i=1, \dots, N-1\}$ is a set of bond vectors in an actual static configuration of the polymer chain, we get:

$$U_1 = \frac{1}{2}(k_0/b_0^2) \sum_{i=1}^{N-1} b_i^{0\alpha} b_i^{0\beta} \delta y_{i\alpha} \delta y_{i\beta} \quad (3)$$

and

$$U_2 = \frac{1}{2}(w/b_0^4) \sum_{i=1}^{N-2} \{ [b_{i+1}^{0\alpha} - (\cos \theta_0) b_i^{0\alpha}] \delta y_{i\alpha} + [b_i^{0\alpha} - (\cos \theta_0) b_{i+1}^{0\alpha}] \delta y_{i+1,\alpha} \}^2 \quad (4)$$

The greek indices designate the space coordinates $\alpha, \beta = 1, \dots, D$, where D is the space dimension.

In the long-wave range the change of the difference δy_i for the index crossing $i \rightarrow i+1$ is very small. Thus it is justified in each case to unite N' monomers ($N'b_0$ small compared to the smallest wave length of interest) into one mass point. Simultaneously we can proceed to a continuous chain.

Using the coefficients of the local configuration, which are symmetric in α and β :

$$\mu_1^{\alpha\beta}(s) = (1/N') \sum_{i=-N'/2}^{N'/2} b_{I+i}^{0\alpha} b_{I+i}^{0\beta} \quad (5)$$

and

$$\mu_2^{\alpha\beta}(s) = (1/2N') \sum_{i=-N'/2}^{N'/2} (b_{I+i+1}^{0\alpha} b_{I+i}^{0\beta} + b_{I+i+1}^{0\beta} b_{I+i}^{0\alpha}) \quad (6)$$

where $I = \text{int}(s/N'b_0)$, it follows for the potential energy in the continuous representation:

$$U = (k_0/2b_0) \int_0^L ds [\mu_1^{\alpha\beta}(s)(1+z) + z\mu_2^{\alpha\beta}(s)] (dy_\alpha/ds)(dy_\beta/ds) \quad (7)$$

Here s is the curve parameter along the chain ($0 \leq s \leq L = Nb_0$) and z , given by:

$$z = 2w(1 - \cos \theta_0)^2 / (k_0 b_0^2) \quad (8)$$

means the ratio of the force constants.

We split up

$$\mu_i^{\alpha\beta} = \langle \mu_i^{\alpha\beta} \rangle + \tilde{\mu}_i^{\alpha\beta} \quad (9)$$

where $\langle \mu_i^{\alpha\beta} \rangle$ is the statistical average of $\mu_i^{\alpha\beta}$ over the ensemble of all possible static chain configurations and the $\tilde{\mu}_i^{\alpha\beta}$ are the deviations of the local configuration coefficients from the configurational averaged values. For a sufficiently large N we can use the central limit theorem and the quantities $\tilde{\mu}_i^{\alpha\beta}$ satisfy a Gauss distribution:

$$P_i = P_{i0} \exp\left(- \sum_{\alpha \geq \beta} (1/2M_{\alpha\beta}^i) \int_0^L ds (\tilde{\mu}_i^{\alpha\beta})^2 \right) \quad (10)$$

which is the measure of the configurational average. Considering the isotropy of our physical problem the dispersion $M_{\alpha\beta}^i$ of the $\tilde{\mu}_i^{\alpha\beta}$ has the following general representation:

$$M_{\alpha\beta}^i = M_1^i \delta_{\alpha\beta} + M_2^i (1 - \delta_{\alpha\beta}) \quad (11)$$

Analogously we must require that the configurational averages of the local configuration coefficients $\mu_i^{\alpha\beta}$ have the form:

$$\langle \mu_i^{\alpha\beta} \rangle = \bar{\mu}_i \delta^{\alpha\beta} \quad (12)$$

which is invariant by a rotation of the coordinate system. By use of the substitution:

$$\begin{aligned} \bar{\chi} \delta^{\alpha\beta} &= (1+z) \langle \mu_1^{\alpha\beta} \rangle + z \langle \mu_2^{\alpha\beta} \rangle \\ \tilde{\chi}^{\alpha\beta}(s) &= (1+z) \tilde{\mu}_1^{\alpha\beta}(s) + z \tilde{\mu}_2^{\alpha\beta}(s) \end{aligned} \quad (13)$$

(by means of which the local configuration coefficients are united in one expression), we find the following equation of motion for the deviation $y_\alpha(s)$ in the continuous chain model:

$$\rho \ddot{y}_\alpha - (k_0/b_0) \{ \bar{\chi} d^2 y_\alpha / ds^2 + d/ds [\tilde{\chi}^{\alpha\beta}(s) dy_\beta / ds] \} = 0 \quad (14)$$

Here $\rho = m_0/b_0$ is the one-dimensional mass density along the chain. Note that all information about the stochastic structure of the static polymer chain is contained in the Gauss-distributed local configuration coefficients $\tilde{\chi}^{\alpha\beta}(s)$.

EIGENVALUE PROBLEM AND SPECTRAL DENSITY

By using the time Fourier-transformed representation of the deviation $y_\alpha(s, t)$:

$$y_\alpha(s, \omega) = (1/2\pi) \int_{-\infty}^{+\infty} y_\alpha(s, t) \exp(i\omega t) dt \quad (15)$$

and the definition of the operator:

$$\hat{B}^{\alpha\beta} = \bar{\chi} \delta^{\alpha\beta} d^2/ds^2 + d/ds [\tilde{\chi}^{\alpha\beta}(s) d/ds] \quad (16)$$

we obtain the Fourier-transformed equation of motion:

$$(\lambda \delta^{\alpha\beta} + \hat{B}^{\alpha\beta}) y_\beta(s, \omega) = 0 \quad (17)$$

in which $\lambda = \rho b_0 \omega^2 / k_0$. The solution of the attached eigenvalue problem $\det[\lambda \delta^{\alpha\beta} + \hat{B}^{\alpha\beta}] = 0$ gives a set of ND/N' eigenvalues λ_i . Note that these eigenvalues have a functional dependence on the topical static structure of the polymer chain.

The spectral density of the frequencies is defined by⁸:

$$g(\omega) = \sum_{i=1}^{ND/N'} \delta(\omega - \omega_i) \quad (18)$$

By application of the relationship between ω and λ we can transform this representation into the ω representation. With the spectral density:

$$G(\lambda) = \sum_{i=1}^{ND/N'} \delta(\lambda - \lambda_i) \quad (19)$$

we get the equation:

$$\omega_0 g(\omega) = 2\lambda^{1/2} G(\lambda) \quad (20)$$

between $g(\omega)$ and $G(\lambda)$. Here, $\omega_0 = (k_0/\rho b_0)^{1/2}$ is the ground frequency of the polymer chain. The calculated spectral densities $g(\omega)$ and $G(\lambda)$, respectively, are functionals of the static chain structure. Physically, we are interested in the configurational average of the spectral density over all possible static chain configurations $\langle g(\omega) \rangle$ and $\langle G(\lambda) \rangle$. This statistical configurational average and its dependence on the frequency is the aim of the following calculations.

For the calculation of the configurational average of the spectral density $G(\lambda)$ for equation (17) we use the fact that for $G(\lambda)$ the identity:

$$\langle G(\lambda) \rangle = (2/\pi) \lim_{\epsilon \rightarrow 0} \text{Im} d/d\lambda \langle \log Z[\lambda] \rangle \quad (21)$$

is known⁹, where $Z[\lambda]$ is given by the functional integral:

$$Z[\lambda] = \int \mathcal{D}y \exp\left(\frac{i}{2} \int_0^L y_\alpha [(\lambda + i\varepsilon)\delta^{\alpha\beta} + \hat{B}^{\alpha\beta}] y_\beta ds\right) \quad (22)$$

Observing the cyclic boundary conditions for the deviation $y_\alpha(s)$ we can transform expression (22) into:

$$Z[\lambda] = \mathcal{N} \int \mathcal{D}y \exp\left(i \int_0^L L_G ds\right) \quad (23)$$

with the Lagrangian:

$$L_G = \frac{1}{2}(\lambda + i\varepsilon)y^2(s) - \frac{1}{2} dy_\alpha/ds [\bar{\chi}\delta^{\alpha\beta} + \tilde{\chi}^{\alpha\beta}(s)] dy_\beta/ds \quad (24)$$

(\mathcal{N} in this case is an inessential constant). For calculating the static configurational average of $\log Z[\lambda]$ we use the replica trick of Edwards¹⁰ and Edwards and Anderson¹¹:

$$\langle \log Z \rangle = \lim_{m \rightarrow 0} \langle (Z^m - 1)/m \rangle = \lim_{m \rightarrow 0} (\langle Z^m \rangle - 1)/m \quad (25)$$

On consideration of (23) and (24) we find for the configurational average of Z^m the expression:

$$\begin{aligned} \langle Z[\lambda]^m \rangle &= \int \mathcal{D}y \exp\left(i \sum_{a=1}^m \int_0^L ds \left[\frac{1}{2}(\lambda + i\varepsilon)y^a(s)^2 - \bar{\chi}(dy^a/ds)^2\right]\right) \\ &\left\langle \exp\left(-i \sum_{a=1}^m \int_0^L ds \tilde{\chi}^{\alpha\beta}(s) (dy_\alpha^a/ds)(dy_\beta^a/ds)\right) \right\rangle \end{aligned} \quad (26)$$

Now it is simple to determine the statistical configurational average in equation (26). By using the Gaussian probability density function (10) we find, after integration over the local configurational coefficients $\tilde{\mu}_i^{\alpha\beta}$:

$$\begin{aligned} \langle Z[\lambda]^m \rangle &= \int \mathcal{D}y \exp\left\{i \sum_{a=1}^m \int_0^L ds \left[\frac{1}{2}(\lambda + i\varepsilon)y^a(s)^2 - \bar{\chi}(dy^a/ds)^2\right] - \int_0^L ds \left[k_1 \sum_{\alpha=1}^D \left(\sum_{a=1}^m (dy_\alpha^a/ds)^2\right)^2 + k_2 \sum_{a,b=1}^m (dy^a/ds dy^b/ds)^2 \right] \right\} \end{aligned} \quad (27)$$

with

$$\begin{aligned} k_1 &= (1+z)^2(M_1^2 - 2M_2^2) + z^2(M_1^2 - 2M_2^2) \\ k_2 &= 2(1+z)^2 M_1^2 + 2z^2 M_1^2 \end{aligned} \quad (28)$$

The M_i^2 are dispersions, which are introduced in equation (11). As a result of this integration, we obtain a coupling between the different replicas in the last two terms of the exponent in equation (27).

THE EXPANDED HARTREE-FOCK APPROXIMATION

We cannot give an exact solution for expression (28). For this reason we must find a reasonable approximation for $\langle Z[\lambda]^m \rangle$. Therefore we transform the exponent of (27) into the Fourier representation with respect to the

curve parameter s :

$$\begin{aligned} L_G &= \frac{1}{2} \sum_{a,\alpha,k} (\lambda + i\varepsilon - k^2 \bar{\chi}) |y_{\alpha k}^a|^2 \\ &- (k_1/2L) \sum_{\alpha} \sum_{a,b,k,k'} \sum_{q,q'} k k' q q' y_{\alpha k}^a y_{\alpha k'}^a y_{\alpha q}^b y_{\alpha q'}^b \delta_{k+k'+q+q',0} \\ &- (k_2/2L) \sum_{\alpha,\beta} \sum_{a,b,k,k'} \sum_{q,q'} k k' q q' y_{\alpha k}^a y_{\alpha k'}^b y_{\beta q}^a y_{\beta q'}^b \delta_{k+k'+q+q',0} \end{aligned} \quad (29)$$

Corresponding to the model discussed in the second section it is necessary to restrict the number of modes to N/N' . Thus the smallest physical length of our model is $l_0 = N'b_0$. In the following calculation we assume that all k modes of the y field are independent. In this case the configurational average between two modes is given by:

$$\langle y_{\alpha k}^a y_{\beta q}^b \rangle = \langle |y_{\alpha k}^a|^2 \rangle \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q} \quad (30)$$

In the well known simple Hartree-Fock approximation¹² we must set:

$$\begin{aligned} y_{\alpha k}^a y_{\beta q}^b &= \langle |y_{\alpha k}^a|^2 \rangle \delta^{ab} \delta_{\alpha\beta} \delta_{kq} \\ &+ (y_{\alpha k}^a y_{\beta q}^b - \langle |y_{\alpha k}^a|^2 \rangle \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q}) \end{aligned} \quad (31)$$

All terms in expression (29) that contain $\Delta_{\alpha\beta kq}^{ab} = (y_{\alpha k}^a y_{\beta q}^b - \langle |y_{\alpha k}^a|^2 \rangle \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q})$ in second or higher order (which does not appear here) are neglected.

In our calculation we use an improvement contrary to this approximation. Instead of expression (31) we set:

$$\begin{aligned} y_{\alpha k}^a y_{\beta q}^b &= |y_{\alpha k}^a|^2 \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q} \\ &+ (y_{\alpha k}^a y_{\beta q}^b - |y_{\alpha k}^a|^2 \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q}) \end{aligned} \quad (32)$$

and neglect all terms that contain $\Delta_{\alpha\beta kq}^{ab} = (y_{\alpha k}^a y_{\beta q}^b - |y_{\alpha k}^a|^2 \delta^{ab} \delta_{\alpha\beta} \delta_{k,-q})$ in second order. Note that in expression (32) in comparison with (31) no configurational averages $\langle |y_{\alpha k}^a|^2 \rangle$ appear.

This expanded Hartree-Fock approximation is reasonable, if the oscillation amplitudes are sufficiently small. (This demand is fulfilled in the low-temperature region.) In the representation (32) the correlation between two differences $\Delta_{\alpha\beta kq}^{ab}$ and $\Delta_{\gamma,\delta k'q'}^{\alpha\beta}$ is the same as in the Hartree-Fock approximation in the non-diagonal case and it vanishes contrary to the Hartree-Fock approximation in the diagonal case.

Then for the first non-quadratic term in expression (29) we get:

$$\begin{aligned} &\sum_{\alpha} \sum_{a,b,k,k'} \sum_{q,q'} k k' q q' y_{\alpha k}^a y_{\alpha k'}^a y_{\alpha q}^b y_{\alpha q'}^b \delta_{k+k'+q+q',0} \\ &= \alpha_{11} \sum_{\alpha,k} \left(\sum_k k^2 |y_{\alpha k}^a|^2\right)^2 + \alpha_{12} \sum_{\alpha,a} \left(\sum_k k^2 |y_{\alpha k}^a|^2\right)^2 \end{aligned} \quad (33)$$

Here α_{11} and α_{12} are mainly arbitrary weight factors that satisfy the condition $\alpha_{11} + \alpha_{12} = 1$. The first term in (33) is proportional to $Dm^2(N/N')^2$, and the second term is proportional to $Dm(N/N')^2$. In the borderline case of $m \rightarrow 0$ (see equation (25)) the first term vanished rapidly in comparison with the second term (see ref. 9). Hence it is reasonable to set $\alpha_{11} = 0$ and $\alpha_{12} = 1$.

Using the approximation (32) the second non-

quadratic term in (29) gives:

$$\begin{aligned} & \sum_{\alpha, \beta} \sum_{a, b} \sum_{k, k'} k k' q q' y_{\alpha k}^a y_{\alpha k'}^b y_{\beta q}^a y_{\beta q'}^b \delta_{k+k'+q+q', 0} \\ &= \alpha_{21} \sum_a \left(\sum_{\alpha, k} k^2 |y_{\alpha k}^a|^2 \right)^2 + \alpha_{22} \sum_a \left(\sum_{\alpha, k} k^2 |y_{\alpha k}^a|^2 \right)^2 \\ & \quad + \alpha_{23} \sum_{\alpha, a} \left(\sum_k k^2 |y_{\alpha k}^a|^2 \right)^2 \end{aligned} \quad (34)$$

Here the arbitrary coefficients are $\alpha_{21} + \alpha_{22} + \alpha_{23} = 1$. The second term is again proportional to $Dm^2(N/N')^2$ and we neglect this contribution ($\alpha_{22} = 0$). The other two terms are proportional to $mD^2(N/N')^2$ and $mD(N/N')^2$, respectively. The weight factors α_{21} and α_{23} remain open, but it is justified to set $\alpha_{21} = \alpha_{23} = \frac{1}{2}$

Considering (33) and (34) the expression (27) now gives:

$$\begin{aligned} \langle Z[\lambda]^m \rangle &= R[\lambda]^m = \left\{ \int \mathcal{D}y \exp \left[\frac{1}{2} i \sum_{\alpha, k} (\lambda + i\varepsilon - k^2 \bar{\chi}) |y_{\alpha k}|^2 \right. \right. \\ & \quad - (k_2/4L) \left(\sum_{\alpha, k} k^2 |y_{\alpha k}|^2 \right)^2 \\ & \quad \left. \left. - [(k_2 + 2k_1)/4L] \sum_{\alpha} \left(\sum_k k |y_{\alpha k}|^2 \right)^2 \right] \right\}^m \end{aligned} \quad (35)$$

Using the integration variables Q and Q' we can transform the expression $R[\lambda]$ into a Gauss-like functional integral with respect to y :

$$\begin{aligned} R[\lambda] &= \int dQ \exp(-\frac{1}{2} \Omega_1 k_2^{-1} L Q^2) \\ & \quad \left[\int dQ' \int \mathcal{D}y \exp \left(\frac{1}{2} i \sum_k [\lambda + i\varepsilon + (2Q + 2Q' - \bar{\chi}) k^2] |y_k|^2 \right. \right. \\ & \quad \left. \left. - \frac{1}{2} \Omega_2 k_2^{-1} L Q'^2 \right) \right]^D \\ &= \int dQ \exp(-\frac{1}{2} k_2^{-1} \Omega_1 L Q^2) \Phi[\lambda, Q]^D \end{aligned} \quad (36)$$

Here, $\Omega_1 = 2$ and $\Omega_2 = 2/(1 + 2k_1/k_2)$.

Now the integration over the y field is trivial. For $\Phi[\lambda, Q]$ we obtain:

$$\begin{aligned} \Phi[\lambda, Q] &= \int dQ' \exp \left(-\frac{1}{2} \Omega_2 k_2^{-1} L Q'^2 \right. \\ & \quad \left. - \sum_{\beta=1}^{N/2N'} \log [\lambda + i\varepsilon - (4\pi^2 \beta^2 / L^2) (\bar{\chi} - 2Q - 2Q')] \right) \end{aligned} \quad (37)$$

In the following calculation we use the density function defined by:

$$\sigma(x) = (N/N') \sum_{\beta=1}^{N/2N'} \delta(x - (4\pi^2 \beta^2 / L^2)) \quad (38)$$

The continuous representation of $\sigma(x)$ is relatively simple to calculate. We obtain:

$$\begin{aligned} \sigma(x) &= [1/(2\pi)] \int_0^{\pi/l_0} \delta(x - k^2) dk \\ &= [1/(4\pi\sqrt{x})] \theta(x) \theta((\pi/l_0)^2 - x) \end{aligned} \quad (39)$$

($\theta(x)$ is the well known Heaviside function). Hence we write for the expression (37):

$$\Phi[\lambda, Q] = \int \exp[-Lg(Q, Q', \lambda)] dQ' \quad (40)$$

with

$$\begin{aligned} g(Q, Q', \lambda) &= \frac{1}{2} \Omega_2 k_2^{-1} Q'^2 \\ &+ \int_0^{(\pi/l_0)^2} [1/(4\pi\sqrt{x})] \log[\lambda + i\varepsilon - x(\bar{\chi} - 2Q - 2Q')] dx \end{aligned} \quad (41)$$

RESULTS

An exact integration of expression (40) by using analytical methods alone is impossible. For a long chain we can find a good approximation for (40). Then we can assume $L \rightarrow \infty$ and the integral can be evaluated by saddle-point integration^{9,13}. We shall consequently retain terms in (40) that are of order $\exp(L)$. The saddle-point equation is given here by:

$$\begin{aligned} dg(Q, Q', \lambda)/dQ' &= \Omega_2 k_2^{-1} Q' \\ &+ (1/2\pi) \int_0^{(\pi/l_0)^2} \sqrt{x} dx [\lambda + i\varepsilon - x(\bar{\chi} - 2Q - 2Q')] = 0 \end{aligned} \quad (42)$$

The solution of this equation is the saddle-point $Q'_s(Q, \lambda)$ and we obtain for (40):

$$\Phi[\lambda, Q] = \Phi_0 \exp[-Lg(Q, Q'_s(Q, \lambda), \lambda)] \quad (43)$$

In the same way we determine $R[\lambda]$ in expression (36). With (43) it follows:

$$iR[\lambda] = \Phi_0 \int dQ \exp \left\{ -L \left[\frac{1}{2} \Omega_1 k_2^{-1} Q^2 + Dg(Q, Q'_s(Q, \lambda), \lambda) \right] \right\} \quad (44)$$

with the pertinent saddle-point equation:

$$\begin{aligned} \Omega_1 k_2^{-1} Q + D[\partial g/\partial Q + (\partial g/\partial Q'_s)(\partial Q'_s/\partial Q)] \\ = \Omega_1 k_2^{-1} Q + D\partial g/\partial Q = \Omega_1 k_2^{-1} Q \\ + (D/2\pi) \int_0^{(\pi/l_0)^2} \sqrt{x} dx \{ \lambda + i\varepsilon - x[\bar{\chi} - 2Q - 2Q'_s(Q, \lambda)] \} = 0 \end{aligned} \quad (45)$$

Note that because of equation (42) the third term of the left-hand side vanishes.

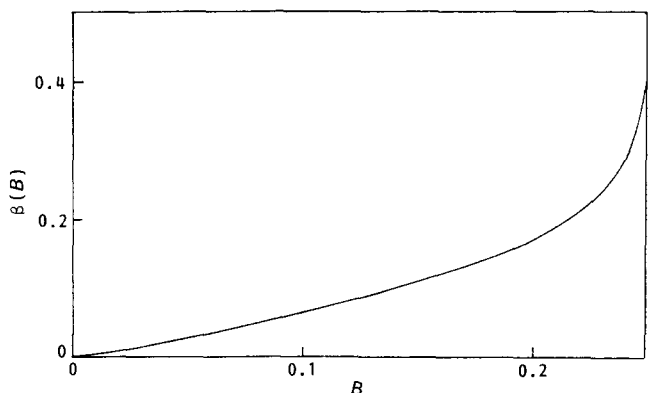
Comparison of (42) and (43) shows that there exists a trivial connection between $Q'_s(Q, \lambda)$ and $Q_s(\lambda)$:

$$Q'_s(Q, \lambda) = (\Omega_1/D\Omega_2) Q_s(\lambda) \quad (46)$$

Now we have an expression for the configurational averaged vibrational density. With (35), (25) and (21) it follows that:

$$\begin{aligned} \langle G(\lambda) \rangle &= (2/\pi) d/d\lambda \text{Im} \log R[\lambda] \\ &= (2L/\pi) \text{Im} [\Omega_1 k_2^{-1} Q_s(\lambda) \partial Q_s(\lambda)/\partial \lambda \\ & \quad + D \{ \partial g/\partial \lambda + (\partial g/\partial Q'_s) [(\partial Q'_s/\partial Q_s)(\partial Q_s/\partial \lambda) + \partial Q'_s/\partial \lambda] \\ & \quad + (\partial g/\partial Q_s)(\partial Q_s/\partial \lambda) \}] \end{aligned} \quad (47)$$

Because of equation (42) the third summand vanishes and because of (45) the first and the last terms drop out.

Figure 1 Function $\beta(B)$

As a result of this calculation and by use of the transformations:

$$\begin{aligned} \eta &= 2(1 + \Omega_1/D\Omega_2)Q_s/\bar{\chi} \\ B &= 2k_2(1/\Omega_2 + D/\Omega_1)l_0^{-1}\bar{\chi}^{-2} \\ \lambda_0 &= \pi^2\bar{\chi}/l_0^2 \end{aligned} \quad (48)$$

we find for the configurational averaged vibrational spectrum the representation:

$$\begin{aligned} \langle G(\lambda) \rangle &= -(LDl_0/\pi^3\bar{\chi}) \operatorname{Im} \int_0^1 dx / [\lambda/\lambda_0 + i\epsilon + x^2(\eta - 1)] \\ &= -(2G_0/\pi) \{ \operatorname{Im} \eta (2 \operatorname{Re} \eta - 1) / [(\lambda/\lambda_0)B] \} \end{aligned} \quad (49)$$

with $G_0 = Ll_0D/2\pi^2\bar{\chi}$ and in which the variable η fulfils the self-consistent integral equation:

$$\begin{aligned} \eta + B/(\eta - 1) &= \\ [B(\lambda/\lambda_0)/(\eta - 1)] \int_0^1 dx / [\lambda/\lambda_0 - x^2(1 - \eta)] \end{aligned} \quad (50)$$

DISCUSSION

Equation (50) is transcendental and so it is clear that we cannot give a general analytic solution. This is possible only in the limit $\lambda \rightarrow 0$. All other results are based on numerical computations.

At first we see that the configurational averaged spectral density $\langle G(\lambda) \rangle$ fulfils the norm condition:

$$\begin{aligned} \int_{-\infty}^{+\infty} \langle G(\lambda) \rangle d\lambda &= (2/\pi) (\operatorname{Im} \log R[\infty]) \\ -\operatorname{Im} \log R[-\infty] &= LD/l_0 \end{aligned} \quad (51)$$

For $\lambda \rightarrow 0$ we find from equation (50):

$$\eta_0 + B/(\eta_0 - 1) = 0 \quad (52)$$

Therefore in this limit:

$$\lim_{\lambda \rightarrow 0} \lambda^{1/2} \langle G(\lambda) \rangle = \lambda_0^{1/2} G_0 \operatorname{Im} [i/(i - \eta_0)^{1/2}] \quad (53)$$

follows.

Note that because of (20) this expression is proportional to $\langle g(\omega \rightarrow 0) \rangle$. So it is possible to write for $\langle G(\lambda) \rangle$:

$$\langle G(\lambda) \rangle = [G_0(\lambda_0/\lambda)^{1/2}] [\beta(B) + r(B, \lambda/\lambda_0)] \quad (54)$$

and

$$\langle g(\omega) \rangle = (2G_0\lambda_0^{1/2}\omega_0) [\beta(B) + r(B, \omega^2/\omega_0^2)] \quad (55)$$

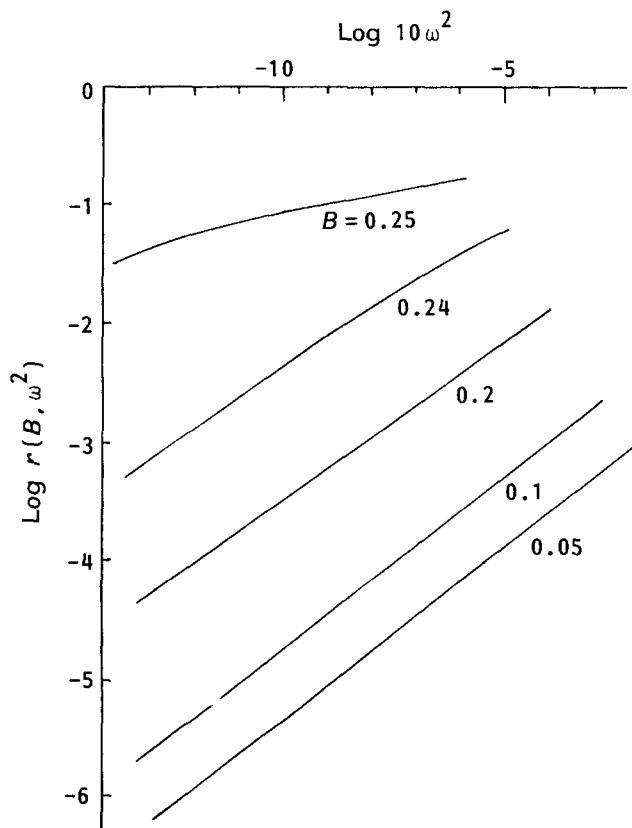
respectively, in which the functions β and r are introduced in a manner such that $\lim r(B, 0) = 0$. Therefore the value $\beta(B)$ describes completely the behaviour of $\langle G(\lambda) \rangle$ in the limit $\lambda \rightarrow 0$. The function $r(B, \lambda)$ determines the deviation of $\langle G(\lambda) \rangle$ from the limit values in the case $\lambda > 0$. Because of (48) the parameter B is a measure of the disorder of the chain structure. (Note that B is proportional to k_1 and k_2 and these values are proportional to the dispersion of the local configuration coefficients $\mu_i^{\alpha\beta}$.)

For $B=0$ we have $\beta(0)=1$ and $r(0, \lambda) \equiv 0$, so that $\lim \langle G(\lambda) \rangle = G_0(\lambda_0/\lambda)^{1/2}$. The function $\beta(B)$ is shown in Figure 1. For small B we found that the increase of $\langle g(\omega) \rangle$ is proportional to the increase of the disorder of the polymer chain, which is given by the parameter B . With (53) we have:

$$\beta(B) = \{2/[1 + (1 - 4B)^{1/2}]\}^{1/2} \quad (56)$$

For $B > 0.25$, $\beta(B)$ decreases with increasing B . But this region is unphysical, because here the stochasticity of the Gauss-distributed local configuration coefficients $\mu_i^{\alpha\beta}$ is so high that in the potential energy (7) negative contributions are possible with a sufficiently large weight. On the other hand the potential energy is a positive definite expression, so that for large Gauss-distributed deviations $\tilde{\mu}_i^{\alpha\beta}$ of the local configuration coefficients from the configurational averages $\langle \mu_i^{\alpha\beta} \rangle$, this demand cannot be met any more.

For small B ($B < 0.25$) the behaviour of $\beta(B)$, which leads to an increase of the density of states at low frequency, is general and can be observed in many disordered systems. A possible explanation of this effect

Figure 2 Function $r(\lambda, B)$ for different $B \leq 0.25$

is given in ref. 14. The function $r(B, \omega^2)$ is obtained by numerical computation for the solution of the transcendental equation (50). Figure 2 shows the results of this numerical examination.

The most important results of this article are the representations (49) and (50) for the configurational averaged vibrational spectral density $\langle G(\lambda) \rangle$, which is only determined by two scaling factors (λ_0 and G_0) and one control parameter B . The value of the smallest physical length $l_0 = N'b_0$, which is contained in all of these quantities, remains to be determined. Here it is reasonable to set $l_0 = l_{\text{eff}}$, where l_{eff} is the effective segment length of the polymer chain. By using the well known relation between the polymer length and the mean-square end-to-end distance $\langle R^2 \rangle$:

$$\langle R^2 \rangle \sim Ll_{\text{eff}}(N_{\text{eff}})^{2r-1} = Ll_{\text{eff}}(L/l_{\text{eff}})^{2r-1} \quad (57)$$

we find:

$$l_0 \sim L(\langle R^2 \rangle / L^2)^{1/[2(1-r)]} \quad (58)$$

Now the vibrational spectrum is determined by molecular parameters (force constants, bond lengths and bond

REFERENCES

- 1 Kirkwood, J. G. *J. Chem. Phys.* 1939, **7**, 506
- 2 Zbinden, R. 'Infrared Spectroscopy of Polymers', Academic Press, New York, 1964
- 3 Mikhailov, D., Zhuravskiy, L. V. and Cheban, Yu. V. 'Progress in Polymer Spectroscopy, Proc. 7th Eur. Symp. on Polymers', Teubner, Leipzig, 1985
- 4 Halley, J. W., Thorpe, M. and Walker, A. *J. Polym. Sci., Polym. Symp.* 1982, **73**, 55
- 5 Helfand, E. *J. Polym. Sci., Polym. Symp.* 1982, **73**, 39
- 6 Helfand, E. and Skolnick, J. *J. Chem. Phys.* 1982, **77**, 5714
- 7 Skolnick, J. and Helfand, E. *J. Chem. Phys.* 1980, **72**, 5489
- 8 Böttger, H. 'Principles of the Theory of Lattice Dynamics', Akademie-Verlag, Berlin, 1983
- 9 Edwards, S. F. and Jones, C. *J. Phys. (A), Math. Gen.* 1976, **9**(19), 1595
- 10 Edwards, S. F. 'Proc. 4th Int. Conf. on Amorphous Materials' (Eds. R. W. Douglas and X. X. Ellis), Wiley, New York, 1970
- 11 Edwards, S. F. and Anderson, P. W. *J. Phys. (F), Metal Phys.* 1975, **5**, 965
- 12 Elk, K. and Gasser, W. 'Die Methode der Greenschen Funktionen in der Festkörperphysik', Akademie-Verlag, Berlin, 1979
- 13 Edwards, S. F. and Warner, M. *J. Phys. (A), Math. Gen.* 1980, **13**, 381
- 14 Handrich, K. and Kobe, S. 'Amorphe Ferro- und Ferrimagnetica', Akademie-Verlag, Berlin, 1980