

Thermal length fluctuations of a linear chain of masses connected by springs in a viscous medium

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By applying the Fluctuation Dissipation Theorem the root mean-square amplitude (RMSA) of the longitudinal vibrations of a linear chain of masses connected by springs in a viscous medium is estimated as a function of the mass of the particles, the force constant of the springs, the number of particles, the damping parameter and temperature. At room temperature the RMS end-to-end length is found to vary from a few tenths of an Angström for hydrocarbon chains of the length found in phospholipid membrane bilayers to several Angströms in α -helices of peptide residues.

1 Introduction

It has been suggested that low-frequency vibrations or bending oscillations in proteins may play a role in their biological activity. The magnitude of the length fluctuations could be a meaningful information carrier.¹ Also it is now widely believed that the electric dipole field of the oriented α -helix in proteins plays a role in catalysis for some enzymes.² Perhaps there is a dynamic aspect of this dipole field since the longitudinal oscillations of the helix will give a varying field that could play a role in catalysis. The calculations of the RMSA of vibrations is a well-documented science for small molecules.³ Peticolas⁴ performed a detailed calculation of the RMSA of vibrations for the lowest frequency of the longitudinal vibrations of linear hydrocarbon chains and α -helix polypeptides without damping. In this paper, we estimate the RMSA with damping as a function of the mass of the particles, the force constant of the springs, the number of particles, the damping parameter and temperature.

In globular proteins the end groups are dynamically active, rather than fixed in space and participate through hydrogen bonding with non-helical segments, in this context both boundary conditions are considered with free and fixed ends.

Damping of the vibrations of polymer chains due to friction with solvent, including hydrodynamic interaction between chain elements have been already considered in ref. 5. The authors concluded that the damping constant is independent of the degree of polymerization. In the present paper we follow an easier method in order to estimate the RMSA of the longitudinal vibrations of a linear chain of masses.

Firstly we estimate the general susceptibility matrix for the normal coordinates of a linear chain of masses connected by springs in a viscous medium in order to apply the Fluctuation Dissipation Theorem (FDT) for estimating the length fluctuations of the linear chain.

2 Electrical and mechanical systems analogies

The establishment of a formal analogy between the differential equations expressing two different types of problems permits a

formal transfer of known solutions of problems of one type to those of the other. The method of complex amplitudes developed in connection with electric circuits has a useful application in mechanical problems where generalized definitions of mechanical impedances or susceptibilities are involved.

The differential equation of a simple (L, R, C)-circuit acted upon by a sinusoidal electromotive force is

$$L \frac{di}{dt} + Ri + \frac{1}{C} \int_0^t idt = E \quad (1)$$

Differentiating eqn. (1) we obtain

$$L \frac{d^2i}{dt^2} + R \frac{di}{dt} + \frac{i}{C} = \frac{dE}{dt} \quad (2)$$

Consider, on the other hand, a mechanical system of a damped oscillator excited by an external sinusoidal force. Its equation is

$$m \frac{d^2x}{dt^2} + b \frac{dx}{dt} + kx = F \quad (3)$$

One observes that eqns. (2) and (3) are of the same form and that the following corresponding quantities indicate the analogy between electrical and mechanical problems:

$$(i, x); \quad (L, m); \quad (R, b); \quad \left(\frac{1}{C}, k\right); \quad \left(\frac{dE}{dt}, F\right) \quad (4)$$

The corresponding electrical, Z_e , and mechanical, Z_m , impedances for both systems are:

$$Z_e = R + i \frac{L}{\omega} (\omega^2 - \omega_{0e}^2) \quad (5)$$

$$Z_m = b + i \frac{m}{\omega} (\omega^2 - \omega_{0m}^2) \quad (6)$$

where i is the imaginary unit, $\omega_{0e} = (1/LC)^{1/2}$ and $\omega_{0m} = (k/m)^{1/2}$ are the corresponding resonance frequencies of the systems.

The corresponding susceptibilities, $\alpha(\omega) = i/\omega Z(\omega)$, are:

$$\alpha_e(\omega) = \frac{(\omega^2 - \omega_{0e}^2) + i\omega\gamma_e}{L[(\omega^2 - \omega_{0e}^2)^2 + (\omega\gamma_e)^2]} \quad (7)$$

$$\alpha_m(\omega) = \frac{(\omega^2 - \omega_{0m}^2) + i\omega\gamma_m}{m[(\omega^2 - \omega_{0e}^2)^2 + (\omega\gamma_m)^2]} \quad (8)$$

where $\gamma_e = R/L$ and $\gamma_m = b/m$ are respectively the electrical and mechanical damping factors or resonance widths.

These electro-mechanical analogies can easily be established for systems with several degrees of freedom. We will use these analogies for estimating the RMSA of the longitudinal vibrations of a linear chain of masses.

3 The fluctuation–dissipation theorem

One way of formulating the FDT is by formally regarding the spontaneous fluctuations of a quantity x as due to the action of some random force f , meaning that the environment senses the system through the *generalized susceptibility*, $\alpha(\omega)$, and responds with a fluctuating force. The Fourier components x_ω and f_ω are related by:

$$x_\omega = \alpha(\omega)f_\omega \quad (9)$$

The relation between the *generalized impedance* $Z(\omega)$ and $\alpha(\omega)$ is:

$$Z(\omega) = \frac{i}{\omega\alpha(\omega)} \quad (10)$$

As $x_\omega = x_{0\omega}e^{-i\omega t}$ we can write:

$$f_\omega = Z(\omega) \frac{dx_\omega}{dt} \quad (11)$$

The spectral densities of the fluctuation are given by

$$(x^2)_\omega = |\alpha(\omega)|^2 (f^2)_\omega \quad (12)$$

The results of the FDT are:

$$(x^2)_\omega = \hbar\alpha''(\omega) \coth \frac{\hbar\omega}{2kT} \quad (13)$$

Correspondingly:

$$(f^2)_\omega = \frac{\hbar\alpha''(\omega)}{|\alpha(\omega)|^2} \coth \frac{\hbar\omega}{2kT} \quad (14)$$

The mean-square of the fluctuating quantity is:

$$\langle x^2 \rangle = \frac{1}{\pi} \int_0^\infty (x^2)_\omega d\omega = \frac{\hbar}{\pi} \int_0^\infty \alpha''(\omega) \coth \frac{\hbar\omega}{2kT} d\omega \quad (15)$$

These formulae constitute the FDT, established by Callen and Welton (1951).⁶ They relate the fluctuations of physical quantities to the dissipative properties of the system. At energies $kT \gg \hbar\omega$ (classical limit) we have $\coth(\hbar\omega/2kT) \approx 2kT/\hbar\omega$, and $|\alpha(\omega)|^2 \approx |\alpha'(0)|^2$. Then eqn. (15) becomes:

$$\langle x^2 \rangle = \frac{2kT}{\pi} \int_0^\infty \frac{\alpha''(\omega)}{\omega} d\omega \quad (16)$$

Using Kramers and Kronig's relationship this integral can be written as:⁷

$$\langle x^2 \rangle = kT|\alpha'(0)| \quad (17)$$

Averaging eqn. (12) in frequency in the classic region, we have:

$$\langle x^2 \rangle = \langle (x^2)_\omega \rangle = \langle |\alpha(\omega)|^2 (f^2)_\omega \rangle \quad (18)$$

and in order for eqns. (17) and (18) to be compatible, we obtain:

$$\langle f^2 \rangle = \frac{kT}{|\alpha'(0)|} \quad (19)$$

From eqns. (17) and (19) we obtain:

$$\langle x^2 \rangle^{\frac{1}{2}} \langle f^2 \rangle^{\frac{1}{2}} = kT \quad (20)$$

This is the classical analogy of the Heisenberg uncertainty principle.¹³ This equation shows a constant equilibrium between the system and the environment, when $\langle f^2 \rangle^{\frac{1}{2}}$ increases in the environment, the systems react in such a way as to inhibit the fluctuation of the corresponding physical quantity x and *vice versa* in order to maintain the product constant equal to kT .

The FDT can be generalised to the case where several fluctuating quantities x_i are considered simultaneously.⁷ In this case, eqns. (13) and (14) have to be replaced by:

$$(x_i x_k)_\omega = \frac{1}{2} i \hbar (\alpha_{ki}^* - \alpha_{ik}) \coth \left(\frac{\hbar\omega}{2kT} \right) \quad (21)$$

$$(f_i f_k)_\omega = \frac{1}{2} i \hbar (\alpha_{ik}^{-1} - \alpha_{ki}^{-1*}) \coth \left(\frac{\hbar\omega}{2kT} \right) \quad (22)$$

with

$$x_{i\omega} = \alpha_{ik} f_{k\omega} \quad f_{i\omega} = \alpha_{ik}^{-1} x_{k\omega} \quad (23)$$

where α_{ki} are the matrix elements of the susceptibility and α_{ki}^* the corresponding complex-conjugate elements.

Electric circuit

Let us give an example of the application of the FDT for the case of one fluctuating variable. The case of several simultaneously fluctuating quantities is the objective of the present work.

In an electric circuit the relation between the Fourier components of the spontaneous fluctuation current I_ω and voltage, V_ω is given by:

$$V_\omega = Z(\omega)I_\omega, \quad (24)$$

Eqn. (24) can be written as

$$q_\omega = \alpha(\omega)V_\omega \quad (25)$$

where q_ω is the Fourier component of the fluctuation charge.

In the case of an *RC* circuit in series, we have

$$Z(\omega) = R - \frac{i}{\omega C} \quad (26)$$

Correspondingly from eqn. (2), $\alpha(\omega)$ is given by:

$$\alpha(\omega) = \frac{-C}{1 + (\tau\omega)^2} + i \frac{\tau\omega C}{1 + (\tau\omega)^2} \quad (27)$$

Then

$$\alpha'(\omega) = \frac{-C}{1 + (\tau\omega)^2}, \quad \alpha''(\omega) = \frac{\tau\omega C}{1 + (\tau\omega)^2} \quad (28)$$

From eqns. (13) and (28) and considering the classical limit, we obtain:

$$(q^2)_\omega = \frac{2kT\tau C}{1 + (\tau\omega)^2} \quad (29)$$

and

$$(V^2)_\omega = \frac{2kT\tau}{C(1 + (\tau\omega)^2)} \quad (30)$$

Then from eqn. (17):

$$\langle q^2 \rangle = kTC \quad (31)$$

Correspondingly the mean quadratic fluctuation of the voltage, $\langle V^2 \rangle = \langle q^2 \rangle C^{-2}$, will be:

$$\langle V^2 \rangle = \frac{kT}{C} \quad (32)$$

For applications of the FDT see refs. 10–18.

4 Coupled oscillators with damping

A system of a chain of N masses m_p each of which is coupled harmonically to its nearest neighbours, is described by the following system of equations

$$\frac{d^2 x_p}{dt^2} + \gamma_p \frac{dx_p}{dt} + \frac{k_p}{m_p} x_p - \frac{k_{p+1}}{m_{p+1}} (x_{p+1} - x_p) = 0 \quad (p = 1, 2, \dots, N) \quad (33)$$

where $\gamma_p = b_p/m_p$ is the damping factor of mass p .

The solutions of eqn. 33, with $\gamma_p = 0$, for a system of N equal particles (mass m) coupled by quasi-elastic forces of constant k per unit displacement, can be written after Born and von Karman⁸ (see also ref. 9) as,

Free ends:

$$x_p = \sum_{j=0}^{N-1} \Theta_{\omega_j} \cos \left[\left(p - \frac{1}{2} \right) \phi_j \right], \quad \omega_j = 2\omega_0 \left| \sin \left(\frac{\phi_j}{2} \right) \right|, \quad (34)$$

$$\omega_0 = \sqrt{\frac{k}{m}}, \quad \phi_j = j \frac{\pi}{N}$$

Fixed ends:

$$x_p = \sum_{j=0}^{N-1} \Theta_{\omega_j} \sin(p\phi_j), \quad \omega_j = 2\omega_0 \left| \sin \left(\frac{\phi_j}{2} \right) \right|, \quad (35)$$

$$\phi_j = j \frac{\pi}{N+1}, \quad j = 1, 2, \dots, N$$

In our case, with damping, Θ_{ω_j} is the j th normal coordinate, solution of the following equation,

$$\frac{d^2 \Theta_{\omega_j}}{dt^2} + \gamma \frac{d\Theta_{\omega_j}}{dt} + \omega_j^2 \Theta_{\omega_j} = 0 \quad (36)$$

with

$$\Theta_{\omega_j} = A_j \exp \left(-\frac{\gamma t}{2} \right) \cos[\omega_j t + \alpha_j] \quad (37)$$

Eqn. (36) is similar to eqn. (12) of ref. 5.

In eqns. (34) and (35), ω_0 has to be replaced by $\omega_{0\gamma}$, namely:

$$\omega_{0\gamma} = \left(\omega_0^2 - \frac{\gamma^2}{4} \right)^{1/2} \quad (38)$$

The decrease in frequency as a result of friction is to be expected, since friction retards motion.

In order to have real frequencies $\omega_0 > \gamma/2 = \tau^{-1}$, where τ is the relaxation time which in accordance to Stokes' law, is given by

$$\tau = \frac{m}{3\pi\eta a} \quad (39)$$

where a is the radius of the spherical particle of mass m and η the viscosity of the medium.

In the case $\omega_0 < \gamma/2$, $\omega_{0\gamma}$ is imaginary and can be written as $\omega_{0\gamma} = i\omega'_{0\gamma}$, with $\omega'_{0\gamma}$ real and given by

$$\omega'_{0\gamma} = \left(\frac{\gamma^2}{4} - \omega_0^2 \right)^{1/2} \quad (40)$$

Then eqn. (37) with $\alpha_j = 0$ transforms in

$$\Theta_{\omega_j} = A_j \exp \left(-\frac{\gamma t}{2} \right) \cos \left[i2\omega'_{0\gamma} \left| \sin \left(\frac{\phi_j}{2} \right) \right| t \right] \quad (41)$$

or

$$\Theta_{\omega_j} = A_j \exp \left(-\frac{\gamma t}{2} \right) \cosh \left[2\omega'_{0\gamma} \left| \sin \left(\frac{\phi_j}{2} \right) \right| t \right] \quad (42)$$

We observe in the former equation that the behavior is not oscillatory, consequently the modes are overdamped.

5 Mean-square amplitudes of the normal coordinates

In order to estimate the length mean-square amplitude, we first calculate the mean-square amplitudes of the normal coordinates.

We have N simultaneously fluctuating quantities, Θ_{ω_j} ($j = 1, 2, \dots, N$), the normal co-ordinates, then the susceptibility matrix is a vector of components,

$$\alpha_{jk} = \alpha_j(\omega) \delta_{jk} \quad (43)$$

$$\alpha(\omega) = [\alpha_1(\omega), \alpha_2(\omega) \dots \alpha_N(\omega)] \quad (44)$$

Following the electro-mechanical analogy, of a series (L,R,C)-circuit for eqn. (36), the corresponding generalized susceptibility $\alpha_j(\omega)$, in accordance with eqn. (8), will be

$$\alpha_j(\omega) = \frac{(\omega^2 - \omega_j^2) + i\omega\gamma}{m \left[(\omega^2 - \omega_j^2)^2 + (\omega\gamma)^2 \right]} \quad (45)$$

The length fluctuations can be expressed in terms of the imaginary components, $\alpha_j''(\omega)$ of the normal coordinates susceptibilities. From eqn. (45) we obtain

$$\alpha_j''(\omega) = \frac{\frac{\gamma}{m} \omega}{(\omega^2 - \omega_j^2)^2 + (\omega\gamma)^2} \quad (46)$$

Applying eqns. (21) and (43), we obtain for the mean correlation of the normal coordinates,

$$\langle \Theta_{\omega_j} \Theta_{\omega_k} \rangle = \frac{i\hbar}{4\pi} \int_{-\infty}^{\infty} (\alpha_k^* - \alpha_j) \delta_{jk} \coth \left(\frac{\hbar\omega}{2kT} \right) d\omega$$

We can observe the only non-null values are given by the mean-square of the normal coordinates ($j = k$), namely,

$$\langle \Theta_{\omega_j}^2 \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \alpha_j''(\omega) \coth \left(\frac{\hbar\omega}{2kT} \right) d\omega \quad (47)$$

In our case, it can be written (see Appendix) as

$$\langle \Theta_{\omega_j}^2 \rangle = \frac{\hbar}{m(4\omega_j^2 - \gamma^2)^{1/2}} \times \frac{\sinh \left[\frac{\hbar}{2kT} (4\omega_j^2 - \gamma^2)^{1/2} \right]}{\cosh \left[\frac{\hbar}{2kT} (4\omega_j^2 - \gamma^2)^{1/2} \right] - \cos \left(\frac{\hbar\gamma}{2kT} \right)} - \frac{2\pi kT\gamma}{m} \sum_{n=0}^{\infty} \frac{n}{\left[\left(\frac{2\pi kT}{\hbar} \right)^2 n^2 + \omega_j^2 \right]^2 - \left(\frac{2\pi kT}{\hbar} \right)^2 \gamma^2 n^2} \quad (48)$$

6 Length mean-square amplitude

As we saw in section 3 the parameters which characterize a thermodynamic system in equilibrium do not generally have precise values, but undergo spontaneous fluctuations. Consider our system in thermal equilibrium, because of thermal fluctuations, the system is constantly absorbing and dissipating

energy, with the mean energy given by,

$$\bar{E} = E_0 \exp(-\gamma t) \quad (49)$$

where E_0 is the initial value of the energy. This is the origin of the length fluctuations (RMSA).

As we mentioned the length RMSA without damping was calculated by Peticolas.⁴ The overall end-to-end length of the linear chain is given by

$$l = x_N - x_1 \quad (50)$$

Accordingly we obtain, using the eqns. (34) and (35)†

Free ends:

$$\langle l^2 \rangle = 4 \sum_{j=0}^{N-1} \langle \theta_{\omega_j}^2 \rangle_{\text{free}} \sin^2 \left(\frac{\pi}{2} j \right) \sin^2 \left[\left(\frac{N-1}{N} \right) \frac{\pi}{2} j \right],$$

$$\omega_j = 2\omega_0 \left| \sin \left(j \frac{\pi}{2N} \right) \right| \quad (51)$$

Fixed ends:

$$\langle l^2 \rangle = 4 \sum_{j=0}^{N-1} \langle \theta_{\omega_j}^2 \rangle_{\text{fixed}} \sin^2 \left[\left(\frac{N-1}{N+1} \right) \frac{\pi}{2} j \right] \cos^2 \left(\frac{\pi}{2} j \right),$$

$$\omega_j = 2\omega_0 \left| \sin \left(j \frac{\pi}{2(N+1)} \right) \right| \quad (52)$$

where we have used the property of the normal coordinates $\langle \theta_{\omega_j} \theta_{\omega_k} \rangle = 0$ if $j \neq k$. In the case of no damping ($\gamma = 0$) we have

Free ends:

$$\langle l^2 \rangle_{\text{free}}^{\gamma=0} = 4 \sum_{j=0}^{N-1} \langle \theta_{\omega_j}^2 \rangle_{\text{free}}^{\gamma=0} \sin^2 \left(\frac{\pi}{2} j \right) \sin^2 \left[\left(\frac{N-1}{N} \right) \frac{\pi}{2} j \right],$$

$$\omega_j = 2\omega_0 \left| \sin \left(j \frac{\pi}{2N} \right) \right| \quad (53)$$

Fixed ends:

$$\langle l^2 \rangle_{\text{fixed}}^{\gamma=0} = 4 \sum_{j=0}^{N-1} \langle \theta_{\omega_j}^2 \rangle_{\text{fixed}}^{\gamma=0} \sin^2 \left[\left(\frac{N-1}{N+1} \right) \frac{\pi}{2} j \right] \cos^2 \left(\frac{\pi}{2} j \right),$$

$$\omega_j = 2\omega_0 \left| \sin \left(j \frac{\pi}{2(N+1)} \right) \right| \quad (54)$$

or (see Appendix)

Free ends:

$$\langle l^2 \rangle_{\text{free}}^{\gamma=0} = \frac{\hbar}{m\omega_0} \sum_{j=0}^{N-1} \coth \left[\frac{\hbar\omega_0 \left| \sin \left(j \frac{\pi}{2N} \right) \right|}{kT} \right]$$

$$\times \frac{\sin^2 \left(\frac{\pi}{2} j \right) \sin^2 \left[\left(\frac{N-1}{N} \right) \frac{\pi}{2} j \right]}{\left| \sin \left(j \frac{\pi}{2N} \right) \right|} \quad (55)$$

Fixed ends:

$$\langle l^2 \rangle_{\text{fixed}}^{\gamma=0} = \frac{\hbar}{m\omega_0} \sum_{j=0}^{N-1} \coth \left[\frac{\hbar\omega_0 \left| \sin \left(j \frac{\pi}{2(N+1)} \right) \right|}{kT} \right]$$

$$\times \frac{\sin^2 \left[\left(\frac{N-1}{N+1} \right) \frac{\pi}{2} j \right] \cos^2 \left(\frac{\pi}{2} j \right)}{\left| \sin \left(j \frac{\pi}{2(N+1)} \right) \right|} \quad (56)$$

Eqn. (55), was given by Peticolas.⁴

† We have also used $\cos A - \cos B = 2\sin \frac{1}{2}(A+B)\sin(B-A)$ and $\sin A - \sin B = 2\sin \frac{1}{2}(A-B)\cos \frac{1}{2}(A+B)$

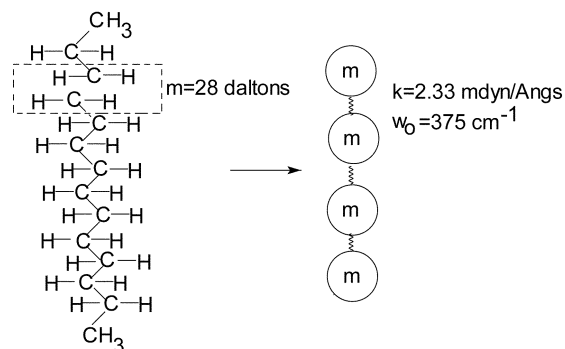


Fig. 1 Schematic model for *trans* hydrocarbons in accordance with Peticolas.⁴

7 Results and discussion

In order to test the model, ω_j from eqns. (34) and (35) with ω_0 given by eqn. (38) and $\phi_j = j(\pi/N)$ or $\phi_j = j[\pi/(N+1)]$, $j = 1, 2, \dots, N$ depending of free or fixed ends has to be fitted against the experimental data of Raman spectroscopy. We suggest performing experiments with decreasing solvent viscosities and extrapolating to zero viscosity (vacuum), in order to obtain ω_0 . Once ω_0 is determined, γ can also be obtained from fitting with the experimental data at a given viscosity.

Once the model is determined, we suggest performing experiments of fluorescence spectroscopy in order to estimate $\langle l^2 \rangle^{1/2}$ for a given peptide configuration varying the viscosity of the medium, see refs. 19–22.

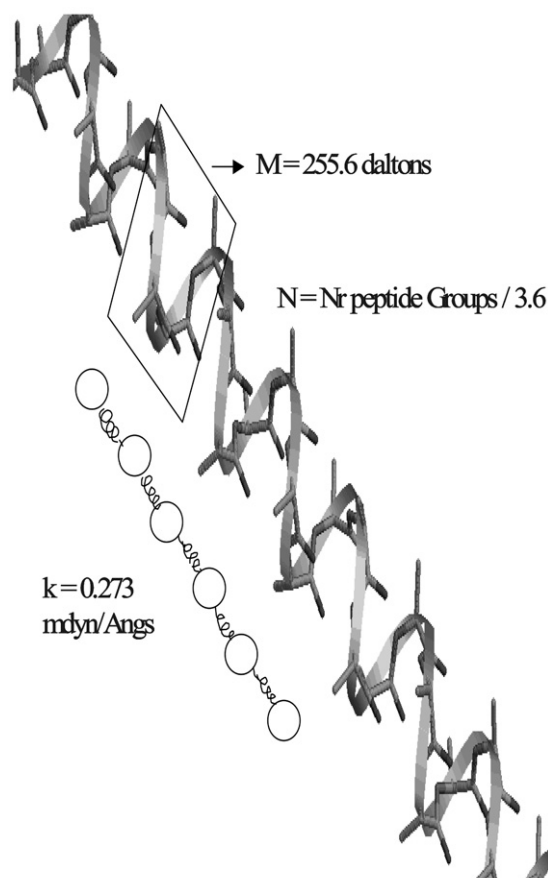


Fig. 2 Schematic model for α -helical poly(L-alanine) in accordance with Peticolas.⁴

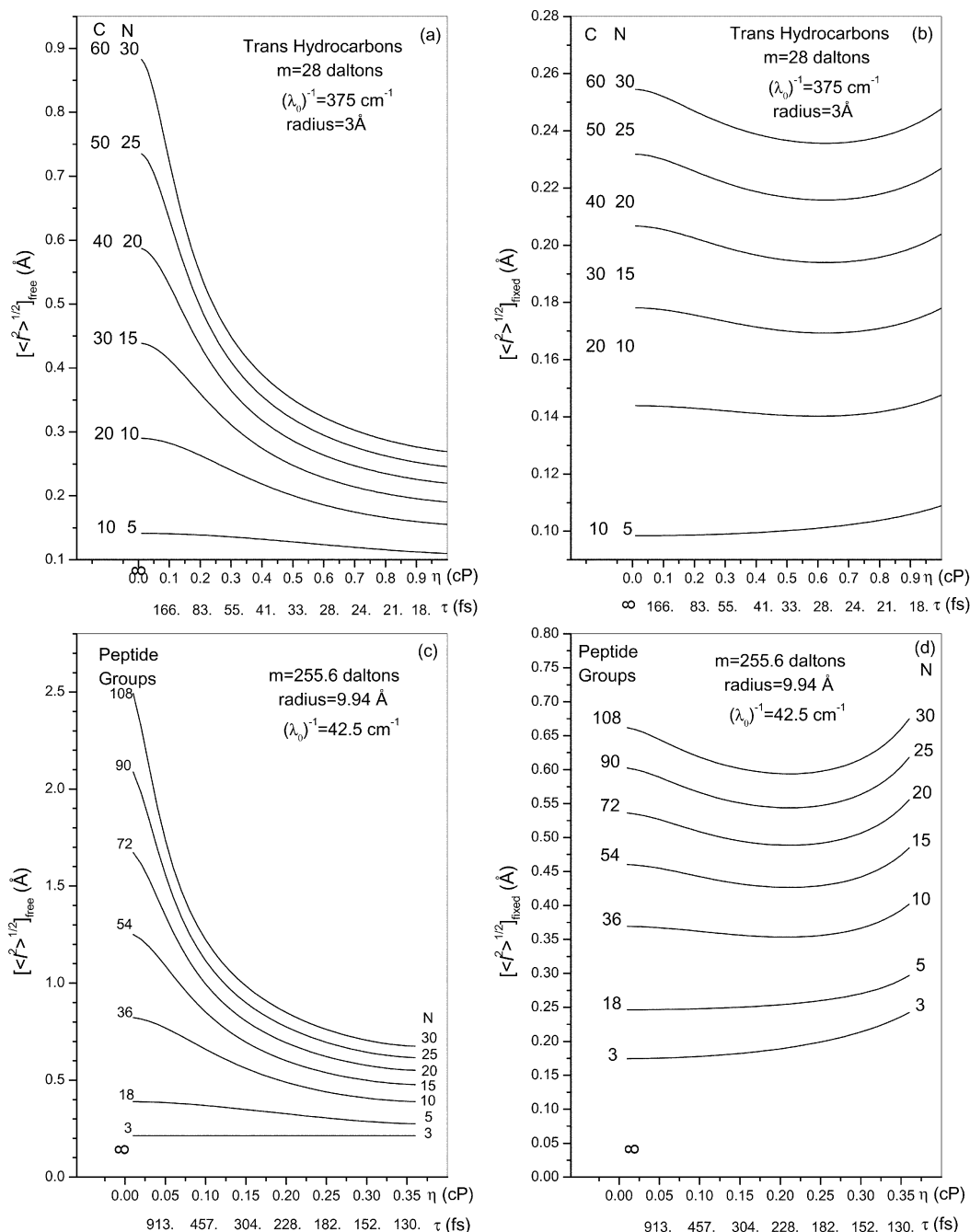


Fig. 3 RMS displacement of the overall end-to-end length, $\langle l^2 \rangle^{1/2}$, at room temperature, of *trans* hydrocarbons and α -helical poly(L-alanine) for free and fixed boundary conditions in accordance to Peticolas' model.⁴

For $\omega_0 \gamma$ real, $\omega_0 > 0.5\gamma = \tau^{-1}$, or in terms of the frequency $f_0 > 0.08\gamma = 0.16\tau^{-1}$, with τ given by eqn. (39). In order to have an idea of the order of magnitude of the relaxation time, we can consider an amino acid residue of 3 Å radius, $m = 100$ Da (1 Da (dalton) = 1.6734×10^{-25} kg) immersed in an environment of viscosity $\eta = 0.1\eta_w$ with η_w being the viscosity of water $\eta_w \simeq 9 \times 10^{-4}$ N s m⁻², we obtain $\tau = 658$ fs or $\tau^{-1} = 1.52 \times 10^{12}$ s⁻¹. If we consider the α -helix oscillations produced by the hydrogen bonds,²⁵ the force constant for the hydrogen bonds is $k = 0.11$ mdyn Å⁻¹ = 11.0 N m⁻¹ in accordance with ref. 23 then $\omega_0 = (km)^{1/2} = 8.1 \times 10^{12}$ s⁻¹. We can observe $\omega_0 > \tau^{-1}$, $\omega_0/\tau^{-1} = 5.3$.

In Figs. 1 and 2 are depicted the models of *trans* hydrocarbons and α -helical poly(L-alanine) in accordance with Peticolas.⁴

In Fig. 3(a–d) is shown the RMS displacement of the overall end-to-end length, $\langle l^2 \rangle^{1/2}$, at room temperature, of *trans* hydrocarbons and α -helical poly(L-alanine) for free and fixed boundary conditions in accordance to the model of Peticolas.⁴ We can observe in both cases, *trans* hydrocarbons and α -helical polypeptide chains, $\langle l^2 \rangle^{1/2}$ decreases with decreasing relaxation time and correspondingly increasing viscosity.

The alkyl chains of fatty acids in lipid bilayer possess the same type of longitudinal acoustical mode as that found in hydrocarbons.²⁴ In Fig. 3(a–b), *trans* hydrocarbons, we observe for $10 \leq \text{carbons} \leq 60$ ($5 \leq N \leq 30$) the corresponding variations of $\langle l^2 \rangle^{1/2}$ are $0.15 \text{ \AA} \leq \langle l^2 \rangle_{\text{free}}^{1/2} \leq 0.9 \text{ \AA}$ and $0.1 \text{ \AA} \leq \langle l^2 \rangle_{\text{fixed}}^{1/2} \leq 0.25 \text{ \AA}$ with the viscosity η and the relaxation time τ varying ($0.0 \text{ cP} \leq \eta \leq 0.9 \text{ cP}$) and ($\infty \leq \tau \leq 18 \text{ fs}$).

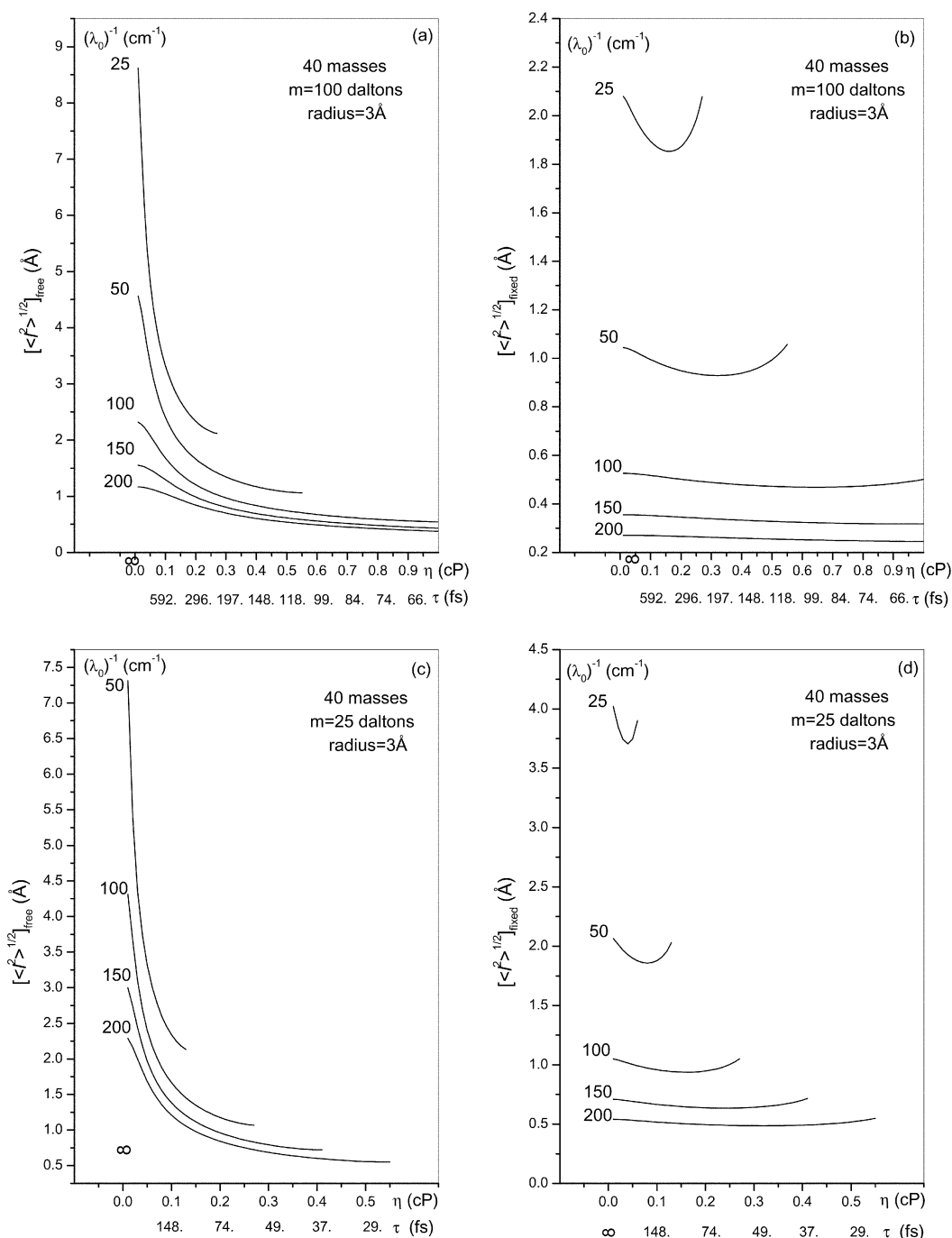


Fig. 4 RMS displacement of the overall end-to-end length, $\langle l^2 \rangle^{1/2}$ for two different chains of 40 masses, at room temperature, for several values of $(\lambda_0)^{-1}$ and for free and fixed boundary conditions.

In Fig. 3(c–d), α -helical polypeptide chains, we observe for peptide groups (PG) varying $3 \leq \text{PG} \leq 108$ ($3 \leq N \leq 30$) the corresponding variations of $\langle l^2 \rangle^{1/2}$ are $0.2 \text{ \AA} \leq \langle l^2 \rangle_{\text{free}}^{1/2} \leq 2.5 \text{ \AA}$ and $0.17 \text{ \AA} \leq \langle l^2 \rangle_{\text{fixed}}^{1/2} \leq 0.67 \text{ \AA}$ with the viscosity η and the relaxation time τ varying ($0.0 \text{ cP} \leq \eta \leq 0.35 \text{ cP}$) and ($\infty \leq \tau \leq 130 \text{ fs}$).

In this last case, we observe a reduced range in the viscosities and correspondingly in the relaxation times because out of this range the modes are overdamped.

In Fig. 4(a–b) are considered chains of 40 masses of 100 Da, each mass with a radius of 3 Å and λ_0^{-1} varying in the range $25 \text{ cm}^{-1} \leq \lambda_0^{-1} \leq 200 \text{ cm}^{-1}$ we can observe, analogously, for low values of λ_0^{-1} a reduced range in the viscosities and correspondingly in the relaxation times because out of this range the modes are overdamped. We can also observe as λ_0^{-1} increases

$\langle l^2 \rangle_{\text{free}}^{1/2}$ decreases. This behaviour is not the same in the case of $\langle l^2 \rangle_{\text{fixed}}^{1/2}$, Fig. 4(b). The corresponding variations of $\langle l^2 \rangle^{1/2}$ in the whole range of considered values of λ_0^{-1} are $1.0 \text{ \AA} \leq \langle l^2 \rangle_{\text{free}}^{1/2} \leq 8.5 \text{ \AA}$ and $0.3 \text{ \AA} \leq \langle l^2 \rangle_{\text{fixed}}^{1/2} \leq 2.1 \text{ \AA}$ with the viscosity η and the relaxation time τ varying ($0.0 \text{ cP} \leq \eta \leq 0.9 \text{ cP}$) and ($\infty \leq \tau \leq 66.0 \text{ fs}$).

In Fig. 4(c–d) are considered chains of 40 masses of 25 Da, each mass with a radius of 3 Å. We observe the case $\lambda_0^{-1} = 25.0 \text{ cm}^{-1}$ for free ends boundary conditions is omitted. This is because ω_r is imaginary and all the modes are overdamped. The rest of the behaviour is similar to Fig. 4(a–b). The corresponding variations of $\langle l^2 \rangle^{1/2}$ in the whole range of considered values of λ_0^{-1} are $0.5 \text{ \AA} \leq \langle l^2 \rangle_{\text{free}}^{1/2} \leq 7.5 \text{ \AA}$ and $0.5 \text{ \AA} \leq \langle l^2 \rangle_{\text{fixed}}^{1/2} \leq 4.0 \text{ \AA}$ with the viscosity η and the relaxation time τ varying ($0.0 \text{ cP} \leq \eta \leq 0.5 \text{ cP}$) and ($\infty \leq \tau \leq 29.0 \text{ fs}$).

8 Appendix

8.1 Normal coordinate mean-square amplitude

We saw that the mean-square of the normal coordinate Θ_j is given by the integral,

$$\langle \Theta_{\omega_j}^2 \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \alpha_j''(\omega) \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega \quad (\text{A-1})$$

In our case we have

$$\langle \Theta_{\omega_j}^2 \rangle = \frac{\hbar\gamma}{2\pi m} \int_{-\infty}^{\infty} \frac{\omega \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega}{(\omega^2 - \omega_j^2)^2 + (\omega\gamma)^2} \quad (\text{A-2})$$

Eqn. (A-2) can be written as

$$\begin{aligned} \langle \Theta_{\omega_j}^2 \rangle &= \frac{\hbar\gamma}{2\pi m} \int_{-\infty}^{\infty} \frac{\omega \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega}{(\omega - \omega_1)(\omega - \omega_2)(\omega - \omega_3)(\omega - \omega_4)} \\ &\equiv \frac{\hbar\gamma}{2\pi m} \int_{-\infty}^{\infty} P(\omega) d\omega \end{aligned} \quad (\text{A-3})$$

The poles of the integrand of eqn. (A-3) are:

$$\begin{aligned} \omega_{1,2} &= i\frac{\gamma}{2} \pm \frac{1}{2} \left(4\omega_j^2 + \gamma^2\right)^{1/2} \\ \omega_{3,4} &= -i\frac{\gamma}{2} \pm \frac{1}{2} \left(4\omega_j^2 - \gamma^2\right)^{1/2} \\ \omega_n &= \frac{2\pi kT}{\hbar} n i = \frac{\pi}{a} n i, \text{ poles of } \coth \end{aligned} \quad (\text{A-4})$$

The corresponding residues in the upper plane are:

$$\begin{aligned} \text{Res}[\omega=\omega_1] &= \frac{\omega_1 \coth(a\omega_1)}{(\omega_1 - \omega_2)(\omega_1 - \omega_3)(\omega_1 - \omega_4)} \\ \text{Res}[\omega=\omega_2] &= \frac{\omega_2 \coth(a\omega_2)}{(\omega_2 - \omega_1)(\omega_2 - \omega_3)(\omega_2 - \omega_4)} \\ \text{Res}[\omega=\omega_n] &= \frac{\pi a^3 n i}{\left[(\pi n)^2 + (a\omega_j)^2\right]^2 - (\pi n a \gamma)^2} \end{aligned} \quad (\text{A-5})$$

8.2 Path integral

For calculating $\langle \Theta_{\omega_j}^2 \rangle$ using eqn. (A-3) we make use of the path integral in the complex plane: we integrate on a closed curve consisting of a semicircle of infinite radius in the upper complex plane, Γ_∞ and the real frequency axis, namely

$$\begin{aligned} I &= \oint_C P(\omega) d\omega \\ &= \int_{\Gamma_\infty} P(\omega) d\omega + \int_{-\infty}^{\infty} P(\omega) d\omega = 2\pi i \sum_C \text{Res} \end{aligned} \quad (\text{A-6})$$

or

$$\int_{\Gamma_\infty} P(\omega) d\omega + \frac{2\pi m}{\hbar\gamma} \langle \Theta_{\omega_j}^2 \rangle = 2\pi i \sum_C \text{Res} \quad (\text{A-7})$$

We will show now that the integral on Γ_∞ goes to zero as the radius of the curve goes to ∞ . Writing $\omega = r \exp(i\theta)$, we obtain

$$\int_{\Gamma} P(\omega) d\omega = i \int_0^\pi \frac{r^2 \exp(i2\theta) \coth[ar \exp(i\theta)] d\theta}{\left[r^2 \exp(i2\theta) - \omega_j^2\right]^2 + \gamma^2 r^2 \exp(i2\theta)} \quad (\text{A-8})$$

The coth can be written as

$$\coth[ar \exp(i\theta)] = \frac{1 + \exp(-2ar \cos \theta) \exp(-i2ar \sin \theta)}{1 - \exp(-2ar \cos \theta) \exp(-i2ar \sin \theta)} \quad (\text{A-9})$$

Taking the limit $r \rightarrow \infty$, we obtain

$$\coth[ar \exp(i\theta)] \leq 1 \Rightarrow \int_{\Gamma} P(\omega) d\omega \leq \lim_{r \rightarrow \infty} i \int_0^\pi \frac{r^2 \exp(i2\theta) d\theta}{O(r^4)} = 0 \quad (\text{A-10})$$

Then using eqn. (A-7)

$$\langle \Theta_{\omega_j}^2 \rangle = i \frac{\hbar\gamma}{m} \sum_C \text{Res} \quad (\text{A-11})$$

From eqns. (A-5) and (A-11) we get

$$\begin{aligned} \langle \Theta_{\omega_j}^2 \rangle &= i \frac{\hbar\gamma}{m(\omega_1 - \omega_2)} \\ &\times \left[\frac{\omega_1 \coth(a\omega_1)}{(\omega_1 - \omega_3)(\omega_1 - \omega_4)} - \frac{\omega_2 \coth(a\omega_2)}{(\omega_2 - \omega_3)(\omega_2 - \omega_4)} \right] \\ &- \frac{\hbar\gamma \pi a^3}{m} \sum_{n=0}^{\infty} \frac{n}{\left[(\pi n)^2 + (a\omega_j)^2\right]^2 - (\pi n a \gamma)^2} \end{aligned} \quad (\text{A-12})$$

Replacing the values for $\omega_j (i = 1 \dots 4)$ given by eqns. (A-4), we obtain[‡]

$$\begin{aligned} \langle \Theta_{\omega_j}^2 \rangle &= \frac{\hbar}{m \left(4\omega_j^2 - \gamma^2\right)^{1/2}} \frac{\sinh\left[\frac{\hbar}{2kT} (4\omega_j^2 - \gamma^2)^{1/2}\right]}{\cosh\left[\frac{\hbar}{2kT} (4\omega_j^2 - \gamma^2)^{1/2}\right] - \cos\left(\frac{\hbar\gamma}{2kT}\right)} \\ &- \frac{2\pi kT\gamma}{m} \sum_{n=0}^{\infty} \frac{n}{\left[\left(\frac{2\pi kT}{\hbar}\right)^2 n^2 + \omega_j^2\right]^2 - \left(\frac{2\pi kT}{\hbar}\right)^2 \gamma^2 n^2} \end{aligned} \quad (\text{A-13})$$

with $\omega_j^2 = 4[\omega_0^2 - (\gamma^2/4)] \sin^2[j(\pi/2N)]$ or $\omega_j^2 = 4[\omega_0^2 - (\gamma^2/4)] \sin^2(j\pi/[2(N+1)])$ depending on having boundary conditions of free or fixed ends respectively. In the case of no damping ($\gamma = 0$), we have respectively $\omega_j^2 = 4\omega_0^2 \sin^2(j\pi/2N)$ and $\omega_j^2 = 4\omega_0^2 \sin^2(j\pi/[2(N+1)])$. Then eqn. (A-13) transforms to give

$$\langle \Theta_{\omega_j}^2 \rangle_{\gamma=0} = \frac{\hbar}{2m\omega_j} \frac{\sinh\left(\frac{2\hbar\omega_j}{2kT}\right)}{\cosh\left(\frac{2\hbar\omega_j}{2kT}\right) - 1} \quad (\text{A-14})$$

or[§]

$$\langle \Theta_{\omega_j}^2 \rangle_{\gamma=0} = \frac{\hbar}{2m\omega_j} \coth\left(\frac{\hbar\omega_j}{2kT}\right) \quad (\text{A-15})$$

Eqn. (A-14) was first obtained by James.²⁶

The second term with the sum (coth terms) in eqn. (A-13) is negligible in most of the real cases, for instance: consider $m = 100$ Da, $\eta_{\text{H}_2\text{O}} \approx 1.0$ cP, $R = 10$ Å, $b = 6\pi\eta_{\text{H}_2\text{O}}R = 18.85 \times 10^{-12}$ N s m⁻¹, $\gamma = b/m = 1.1287 \times 10^{14}$ s⁻¹, for $\omega_j = 3 \times 10^{12}$ s⁻¹, we obtain $\langle \Theta_{\omega_j}^2 \rangle_{\text{coth terms}} = 7 \times 10^{-39}$ m².

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[‡] Where we have used the relation $\coth(x \pm iy) = (\sinh 2x \mp i \sin 2y) / (\cosh 2x - \cos 2y)$.

[§] Where we have used the relation $\cosh(2x) - 1 = 2\sinh^2 x$ and $\sinh 2x = 2\sinh x \cosh x$.

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