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Research Article

Quantized Constrained Molecular Chains: Vibrations, Internal Rotations and Polymerization

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Abstract: The present work has a twofold purpose. a) It proposes a quantum-mechanical approach to constrained molecular chains and their small vibrations and rotations, by employing in a compact way vector variables and operators associated to the constituent units of the chain. The methods here differ from standard approaches based upon cartesian coordinates and normal modes and generalize previous quantum Hamiltonians describing only rotational degrees of freedom. Several models in $D = 2, 3$ spatial dimensions, with new Hermitean Hamiltonians, are formulated and analyzed. The chains studied successively display an increasing number of constraints: freely-jointed, freely-rotating and with constrained torsions. Conservation of total orbital angular momentum is analyzed. As a partial test, by using the present approach, the vibrational frequencies of certain triatomic molecules (water vapour, hydrogen sulfide, heavy water and sulfur dioxide) are computed and shown to be consistent with experimental data. b) A new (quantum-mechanical) analysis of polymerization, namely, the growth of a freely-jointed molecular chain (of the kind considered above) by binding an additional unit 1 to the chain, is presented. They move in a very dilute solution in a fluid at rest in thermal equilibrium about room temperature. The analysis is based upon a mixed (quantum-classical) distribution function in phase-space: a quantum Wigner-like one for unit 1 and a classical Liouville one for the chain. That leads to an approximate Schmolukowski equation for unit 1 alone and, through it, to compute the mean first passage time (MFPT) for unit 1 to become bound by the chain. The resulting MFPT displays a temperature dependence consistent with the Arrhenius formula for rate constants in chemical reactions.

***Keywords*:** constrained molecular chains, freely-jointed, freely-rotating, quantum hermitean hamiltonians, polymerization

MSC: 35J10, 81S30, 81V55, 82D60, 92E10, 92C40

1. Introduction

1.1 *General features and overview*

In various ranges of absolute temperature T in an interval about room temperature, certain degrees of freedom in molecular chains are constrained by strong (covalent) forces. Specifically, by assumption, $K_B T$ (K_B being Boltzmann constant) is adequately smaller than typical electronic energies E_{el}. In this work, the words "molecular chains" will

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be employed independently of the number of constituent units along it. Molecular chains formed by N units will be considered: monomers, small molecules, atoms. all possibilities being encompassed, depending on the context, just by denoting them generically “units”. In those ranges of T, the constituent units (monomers, small molecules, atoms) in the molecular chain have unaltered inner structures, behave essentially as single entities and keep their individuality. Such individuality enables not to worry about molecular features which are not altered in some given phenomena and temperature ranges and to concentrate on the remaining degrees of freedom in the molecular chain which do change. Possible changes of the latter may include, among others, chemical reactions (involving only electrons in external atomic shells in certain constituent units), leading to the eventual formation or destruction of some bond. This standpoint suffices, generally speaking, for treating chemical and biochemical processes at those ranges of T [1-5].

Molecular and macromolecular chains provide the basis for vast, diversified and very important fields, interrelated among themselves (see [3, 5] to which one may add, for instance, polymer science [6]). Constraints (of those degrees of freedom which either do not change or suffer small changes) in molecular chains are at the root of important phenomena of molecular physics: for instance, vibrations. The basis for the study of those phenomena in constrained molecular chains is provided by quantum mechanics.

To the best of the author’s knowledge, standard quantum-mechanical analysis of vibrations in molecules assume usually from the outset constrained distances and angles and concentrates on small deviations and vibrations about the latter (extending, in turn, standard approaches to vibrations in crystals [7]). Thus, for instance, molecular vibrations in molecules are dealt with at length in [8], [9] while vibrations in biological macromolecules, specifically in DNA, are studied in [10-11]. It is emphasized that those standard approaches are based generically on cartesian coordinates and normal modes and (except for a few exceptions) appear to make no use of vector variables and operators associated to the constituent units of the chain.

In different situations, it is possible to bypass approximately the quantum mechanical description and to employ classical mechanics one and, even, probabilistic ones.

Thus, as formulated and employed currently, chemical kinetics employs effective rate equations [2, 12-13] in which rate constants appear explicitly, omitting their connections to quantum-mechanical quantities. However, for instance, one should also remember the well known Transition State Theory of chemical reactions which, even if employing rate equations, makes, in certain formulations and at certain stages, a direct appeal to quantum mechanics [14]. Then, when chemical reactions are involved, something, at least, from the quantum approach may be required unavoidably at some stage for a deeper understanding.

Other important approaches are based upon classical statistical mechanics, still with some quantum-mechanical additions, and are aimed at describing properties of chemical interest: see, for instance [15].

Vast phenomena and properties of polymers can be accounted for combining phenomenological, chemical and thermodynamical developments [6]. Different well-established studies on macromolecular chains (polymers, biopolymers) are based upon phenomenological and probabilistic approaches: the standard Gaussian model for freely jointed polymer chains as random walks and modifications thereof, like the extension for freely-rotating chains (including persistent lengths to approximate constrained angles between neighbouring bonds)…. Such models do provide useful approximations for real single polymer chains (under various conditions, for instance, when excluded volume effects can be neglected) [1, 16]. See also [17-19]. For theoretical approach employing functional integrals, see [20]. Various quantum-mechanical approaches, from standpoints different from the ones developed in the present work, can be seen in [21-24].

The very addition of one additional unit to a molecular chain (polymerization) can be currently analyzed through direct and standard thermodynamical and kinetic approaches [6]. However, since polymerization amounts to a chemical reaction, one may expect that certain genuine quantum-mechanical features in it would eventually require a deeper analysis.

1.2 *Previous quantum models for constrained molecular chains*

In previous works [25-31], quantum models were formulated for $3D$ molecular chains and polymers at thermal equilibrium (supposedly, in solution in a fluid at thermal equilibrium). In particular, variational computations in [25, 27, 29-31] led to certain quantum Hamiltonian for freely-jointed molecular whains (which will also be derived in Eq. (34) in subsection 4.1 of the present work). In [32] a detailed (approximate) analytical computation in the classical limit lead from that Hamiltononian (identical to Eq. (34)) for a polymer at thermal equilibrium just to the standard Gaussian model and some of its properties. Furthermore, in [27] an extension for a freely-rotating chain of the approximations in [32], led to obtain a persistent length, in approximate consistency with [1, 16]. This indicated that that quantum approach has consequences which do approximate the behaviour of real polymers. Application of those variational quantum-mechanical techniques led to an approximate model for DNA [33]. In turn, based upon the latter, a generalized Gaussian model with suitable interactions included led to a model for DNA thermal denaturation and consistent predictions for its time duration [34].

In those works [25, 27-31, 33], the resulting quantum Hamiltonians after the variational computations only included rotational degrees of freedom, but not vibrational ones. They did not allow either the possibility of discussing chemical reactions (for instance, polymerization). The present work will be devoted to extensions of those models to deal with those two issues.

1.3 *New quantum models in the present work*

The present work has a dual purpose.

a) It will generalize non-trivially the quantum models reminded in the previous subsection [25, 27-31], in which small vibrations about constrained coordinates were not easy to analyze. So, a new but related quantum-mechanical approach will be proposed in which small vibrations and rotations in constrained molecules can be analyzed systematically. In so doing, from the outset vector variables and operators associated to the constituent units of the chain, which will provide compact and economical descriptions, are employed. Thus, the present work does not rely upon cartesian coordinates and normal modes. That will display several advantages (for instance, conservation of total orbital angular momentum). As particular cases aimed to test the consistency of the formalism, some triatomic molecules will be treated.

b) It will provide a new fresh (quantum-mechanical) look at dynamical processes like polymerization, namely, the growth of the molecular chain in a fluid, in a simplified case.

Both purposes are strongly interrelated: the study of polymerization in a chain will require some previous model for the latter. In particular, upon developing b), use will be made of the $3D$ model in [25, 27, 29-31] and in Eq. (34) (subsection 4.1 of the present work), in the classical limit.

Various chains with increasing complexity will be treated, so as to proceed to dynamical processes in a later section. For the sake of readability, Sections 2-5 will present the main developments, by omitting many technical aspects and several complicated constructions, which are summarized in Appendixes A-L. Useful formulae helpful in building up the new models are summarized in Appendix A. Section 2 outlines some essentials on Quantum Mechanics and vector formulations for three-dimensional ($3D$) and two-dimensional ($2D$) chains, as a basis for the new developments in the present work. Section 3 present new vector approaches to small vibrations about constrained coordinates in $2D$ freely-jointed (fj) and freely-rotating (fr) chains. Section 4 generalizes Section 3 to the more difficult $3D$ fj and fr chains. As examples and new results, the corresponding Schrodinger equations for fj chains for $N = 2$ are solved in outline for D = 2 and D = 3 in Appendixes B and C, respectively. Appendix F deals with the $D = 2$ fr chain for $N = 3$. Section 5 treats quantum-mechanically a dynamical process: polymerization of a fj chain. Variational consistency checks of the models for fj chains in Sections 3 and 4 are outlined in Appendixes D and E. Appendixes G and H, by reminding potentially interesting results from previous variational computations on constraints in $3D$ fr chains [29-31], lead to new effective Hamiltonians. Appendix I deals with total orbital angular momentum for $3D$ chains. Appendix J summarizes useful computations employed in Section 5. For completeness, Appendices K and L treat succinctly $3D$ chains with vibrations and torsional constraints and branched chains, respectively.

Sections 2, 3 and 4 are written, by omitting most computational details, which are collected in all Appendices except in Appendix J. In turn, Section 5 describes the main lines in the argument, while most computational details are outlined in Appendix J.

A general comment about subscripts will be in order (of course, to be adequately interpreted, depending on the context). The first subscript will indicate the spatial dimension: $D = 2, 3$. Subscripts fj, fr, v, τ will refer to specific chains: freely-jointed, freely-rotating, inclusion of vitrations, torsional constraints, respectively, and so on. The last subscript in some dynamical variable will remind the unit to which that variable is associated to.

2. 3D and 2D open linear chains: general aspects

In three-dimensional (3D) space, one considers a system of N non-relativistic units, with masses M_i, forming an open linear molecular chain. Let $\mathbf{R}_i$, $\mathbf{R}_{CM}$ and $\mathbf{y}_i$ ($1 \leq i \leq N-1$) be the position vectors of the units, of the center-of-mass (CM) and the relative ones for the units, respectively. One has: $\mathbf{R}_{CM} = M^{-1}\sum_{i=1}^{N} M_i\mathbf{R}_i$ and $\mathbf{y}_i = \mathbf{R}_{i+1} - \mathbf{R}_i$ ($M = \sum_{i=1}^{N} M_i$).

The quantum Hamiltonian operator is: $\tilde{H}_1 + E_{el}$, $\tilde{H}_1 = -\sum_{i=1}^{N}(\hbar^2/2M_i)(\nabla_i)^2 + U$. $\hbar$ is Planck's constant and ∇ is the gradient operator. For notational simplicity, ∇_i is understood to denote the gradient with respect to $\mathbf{R}_i$. The molecular chain is treated in the framework of the Born-Oppenheimer approximation [4], so that the (most rapidly-varying) electronic degrees of freedom have already been integrated out and their effect is accounted for by $E_{el} + U$. E_{el} (< 0) is the electronic energy (essentially, a constant), which will always be substracted. U is the remaining (real) potential energy. The degrees of freedom associated to $\mathbf{R}_{CM}$ are factored out. One gets: $\tilde{H}_1 = -(\hbar^2/2M)(\nabla_{\mathbf{R}})^2 + \tilde{H}$, with ($\mathbf{y} \equiv (\mathbf{y}_1, \mathbf{y}_2, \ldots, \mathbf{y}_{N-1})$):

$$\tilde{H} = -\frac{\hbar^2}{2}\sum_{i,j=1}^{N-1} A_{ij}\nabla_{\mathbf{y}_i}\nabla_{\mathbf{y}_j} + U(\mathbf{y}). \tag{1}$$

Also for notational simplicity, $\nabla_{\mathbf{R}}$ denotes the gradient with respect to $\mathbf{R}_{CM}$. The constants A_{ij} are given by: $M_i^{-1} + M_{i+1}^{-1}$ if $i = j$, $-M_i^{-1}$ if $j = i-1$, $-M_j^{-1}$ if $j = i+1$, and 0, otherwise. $U(\mathbf{y})$ is independent on $\mathbf{R}_{CM}$ and depends on absolute values of linear combinations of $\mathbf{y}_l$ (like $|\mathbf{y}_j|$, $|\mathbf{y}_j + \mathbf{y}_l|$ and so on). In 3D spherical coordinates, threemomentum operators read:

$$-i\hbar\nabla_{\mathbf{y}_i} = -\frac{\mathbf{a}_{3,i}}{y_i} - i\hbar\mathbf{u}_i\frac{\partial}{\partial y_i}, \tag{2}$$

$$\mathbf{y}_i = y_i\mathbf{u}_i,\ \mathbf{a}_{3,i} = i\hbar\mathbf{u}_{\theta_i}\frac{\partial}{\partial\theta_i} + i\hbar\mathbf{u}_{\varphi_i}\frac{1}{\sin\theta_i}\frac{\partial}{\partial\varphi_i}, \tag{3}$$

$$\mathbf{u}_i = \left(\cos\varphi_i\sin\theta_i,\ \sin\varphi_i\sin\theta_i,\ \cos\theta_i\right), \tag{4}$$

$$\mathbf{u}_{\theta_i} = \left(\cos\varphi_i\cos\theta_i,\ \sin\varphi_i\cos\theta_i,\ -\sin\theta_i\right), \tag{5}$$

$$\mathbf{u}_{\varphi_i} = \left(-\sin\varphi_i,\ \cos\varphi_i,\ 0\right). \tag{6}$$

The vectors $\mathbf{u}_i$, $\mathbf{u}_{\varphi_i}$, $\mathbf{u}_{\theta_i}$ constitute an orthonormal set. Let:

$$\mathbf{e}_{3,l} \equiv i\hbar\mathbf{u}_l - \mathbf{a}_{3,l}, \tag{7}$$

$l = 1, \ldots, N-1$ [26, 29-30]. Let $\prod_{l=1}^{N-1} d^3\mathbf{y}_l = \prod_{l=1}^{N-1} y_l^2 dy_l[\mathbf{d\Omega}]_3$, $[\mathbf{d\Omega}]_3 \equiv \prod_{l=1}^{N-1} d\varphi_l d\theta_l \sin\theta_l$. Let $\theta \equiv (\theta_1, \ldots, \theta_{N-1})$, $\varphi \equiv (\varphi_1, \ldots, \varphi_{N-1})$. The 3$D$ scalar product of two wavefunctions ψ_j, $j = 1, 2$, depending on all $\mathbf{y}_l$, $l = 1, \ldots N-1$ reads:

$$(\psi_1, \psi_2)_3 \equiv \int \prod_{l=1}^{N-1} y_l^2 dy_l [\mathbf{d\Omega}]_3 \psi_1^* \psi_2 , \tag{8}$$

the integration being carried out over any $\mathbf{y}_l$, $l = 1, \ldots N-1$, and $*$ denoting complex conjugate. An important property is the Hermiticity of both $\mathbf{e}_{3,l}$ and $\tilde{H}$ with the scalar product in Eq. (8).

Let $\mathbf{l}_i = -i\hbar \mathbf{u}_{\varphi_i} \frac{\partial}{\partial \theta_i} + i\hbar \mathbf{u}_{\theta_i} \frac{1}{\sin\theta_i} \frac{\partial}{\partial \varphi_i}$ be the i-th $3D$ orbital angular momentum operator (associated to $\mathbf{u}_i$) and let $\mathbf{L}_3 = \sum_{i=1}^{N-1} \mathbf{l}_i$ be the total $3D$ orbital angular momentum. It commutes with $\tilde{H}$ ($[A, B] \equiv AB - BA$, for any operators A, B): $[\tilde{H}, \mathbf{L}_3] = 0$.

In $2D$ standard polar coordinates, the Hamiltonian is also given in Eq. (1), with:

$$-i\hbar \nabla_{\mathbf{y}_i} = -\frac{\mathbf{a}_{2,i}}{y_i} - i\hbar \mathbf{u}_i \frac{\partial}{\partial y_i}, \mathbf{y}_i = y_i \mathbf{u}_i , \tag{9}$$

$$\mathbf{a}_{2,i} = i\hbar \mathbf{u}_{\varphi_i} \frac{\partial}{\partial \varphi_i}, \mathbf{u}_i = \left(\cos\varphi_i, \sin\varphi_i\right), \mathbf{u}_{\varphi_i} = \left(-\sin\varphi_i, \cos\varphi_i\right) \tag{10}$$

The vectors $\mathbf{u}_i$, $\mathbf{u}_{\varphi_i}$, constitute an orthonormal set. There are $N-1$ angular variables in $(\varphi_1, \ldots, \varphi_{N-1}) = \varphi$. Let:

$$\mathbf{e}_{2,l} \equiv \frac{i\hbar \mathbf{u}_l}{2} - \mathbf{a}_{2,l} = (e_{2,i,x}, e_{2,i,y}), l = 1, \ldots, N-1. \tag{11}$$

The $2D$ scalar product is given by the right-hand-side (rhs) of Eq. (8), now with $\prod_{l=1}^{N-1} d^2\mathbf{y}_l = \prod_{l=1}^{N-1} y_l dy_l [\mathbf{d\Omega}]_2$, $[\mathbf{d\Omega}]_2 \equiv \prod_{l=1}^{N-1} d\varphi_l$. The Hamiltonian and $\mathbf{e}_{2,l}$ are Hermitean under Eq. (8). Let $l_i = -i\hbar \frac{\partial}{\partial \varphi_i}$ be the i-th orbital angular momentum operator, associated to $\mathbf{u}_i$. Let $L_2 = \sum_{i=1}^{N-1} l_i$ be the total orbital angular momentum. A curious property is the set of commutation relations: $[e_{2,i,x}, e_{2,i,y}] = -i\hbar l_i$, $[e_{2,i,x}, l_i] = -i\hbar e_{2,i,y}$, $[e_{2,i,y}, l_i] = i\hbar e_{2,i,x}$. By using them, it follows that L_2 commutes with the $2D$ $\tilde{H}$.

3. 2D open linear chains including small vibrations

New models for $2D$ freely-jointed and freely-rotating molecular chains with small vibrations will be presented in this Section, involving various approximations.

3.1 *2D freely-jointed with vibrations*

Let, as a dominant effective approximation of the covalent bonding (neglecting other interactions), nearest-neighbour atoms interact through harmonic-oscillator-like potentials $V_j = (2A_{jj})^{-1} \omega_{0,j}^2 (y_j - d_j)^2$ ($y_j = |\mathbf{y}_j|$) with vibrational frequencies $\omega_{0,j}$ and bond lengths d_j [29]. Then, one approximates: $U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j$. In latter sections further nondominant contributions to $U(\mathbf{y})$ will be included. Let the frequencies $\omega_{0,j}$ (with $\hbar\omega_{0,j}$ much smaller than E_{el}) be somewhat (but not much) larger than some energy scale (for instance, $K_B T$). One is also assuming that, on that energy scale, angular degees of freedom are not contrained. In such a regime, on physical grounds one expects that y_j equals, approximately the constant distance d_j (bond length), except for some small (radial) variable displacement x_l : $y_j = d_j + x_j$, with $|x_j| \ll d_j$.

Let: $x = (x_1, \ldots, x_{N-1})$. Then, the following approximations will enable to proceed from the 2D counterpart of Eq. (1) to a new model. Variables will be changed as follows: $(y_l, \varphi_l) \to (x_l, \varphi_l)$, $l = 1, \ldots, N-1$. Also: $\prod_{l=1}^{N-1} d^2\mathbf{y}_l \to \prod_{l=1}^{N-1} d_l dx_l [\mathbf{d\Omega}]_2$, $\int_0^{+\infty} y_l dy_l \to \int_{-\infty}^{+\infty} d_l dx_l$, $1/y_l \to 1/d_l$, $\partial/\partial y_l \to \partial/\partial x_l$, $V_j \to V_{fjv,j} = (2A_{jj})^{-1}\omega_{0,j}^2 x_j^2$.

The molecular chain with those small radial vibrations is described by wavefunctions: $\psi = \psi(x, \varphi)$. Let the new global 2D scalar product of two wavefunctions ψ_j, $j = 1, 2$ and 2D "momentum" operator be:

$$(\psi_1, \psi_2)_{2,fjv} \equiv \int_{-\infty}^{+\infty} \prod_{l=1}^{N-1} d_l dx_l \int [\mathbf{d\Omega}]_2 \psi_1(x, \varphi)^* \psi_2(x, \varphi), \tag{12}$$

$$\boldsymbol{\pi}_{2,fjv,i} = -i\hbar \frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{2,i}}{d_i}. \tag{13}$$

$\mathbf{e}_{2,i}$ is given in Eq. (11). The following approximate Hamiltonian describing small "radial" vibrations about constrained distances along the 2D freely-jointed molecular chain will be assumed, suggested by the 2D counterpart of Eq. (1):

$$\tilde{H}_{2,fjv} = \frac{1}{2}\sum_{i,j=1}^{N-1} A_{ij}\boldsymbol{\pi}_{2,fjv,i}\boldsymbol{\pi}_{2,fjv,j} + U_{fjv},\ U_{fjv} = \sum_{j=1}^{N-1} V_{fjv,j}. \tag{14}$$

An important property is the Hermiticity of any $\boldsymbol{\pi}_{2,fjv,i}$ and $\tilde{H}_{2,fjv}$ with the global 2D scalar product in Eq. (12). The total orbital angular momentum L_2 given in Section 2 commutes with the 2D $\tilde{H}_{2,fjv}$. The purely angular motion of the freely jointed molecular chain is described by the x-independent part of $\tilde{H}_{2,fjv}$:

$$\tilde{H}_{2,fj} = \sum_{i,j=1}^{N-1} \frac{A_{ij}}{2d_i d_j}\mathbf{e}_{2,i}\mathbf{e}_{,j} \tag{15}$$

and by wavefunctions $\psi = \psi(\varphi)$, eigenfunctions of the stationary Schrodinger equation, with energy eigenvalues E:

$$\tilde{H}_{2,fj}\psi = E\psi. \tag{16}$$

See Appendix B for common 2D eigenfunctions of $\tilde{H}_{2,fj}$ and L_2 for $N = 3$. The consistency of these new models will be outlined in Appendixes D and E. These 2D fj chains will facilitate the understanding of the 3D fj chains in Subsection 4.1.

3.2 2*D* freely-rotating with vibrations

Let an energy scale (say, K_BT) adequately smaller than that considered in Subsection 3.1 be considered. Then, forces between pairs of next-to-nearest-neighbour units may be strong enough to restrict the corresponding distances to fixed values, with allowance for small oscillations about them: they approximate the covalent bonding due to successive single pairs of shared electrons [3, 15]. Example: polyethilene. Thus, let the potentials between units which are next-to-nearest neighbours be: $V^{(2)}_{j,j+1} = 2^{-1} B_{j,j+1}\omega^2_{0,j,j+1}(d_j d_{j+1}/d_{j,j+1})^2(\beta_{jj+1} - \beta^{(0)}_{j,j+1})^2$. $\omega_{0,j,j+1}$ are other frequencies, $d_{j,j+1}$ are lengths such that $|d_j - d_{j+1}| \le d_{j,j+1} \le d_j + d_{j+1}$ and $B_{j,j+1}(M^{-1}_j + M^{-1}_{j+2}) = 1$.

For suitably large $\omega_{0,j,j+1}$, $\sum_{j=1}^{N-2} V^{(2)}_{j,j+1}$ hinders part of the allowed internal rotations in the molecular chain. Then, the angles between $\mathbf{y}_j$ and $\mathbf{y}_{j+1}$, $j = 1, \ldots, N-2$, are also approximately contrained. It will be convenient to introduce, in general ($j = 1, \ldots, N-2$) $|\mathbf{y}_j + \mathbf{y}_{j+1}| = [y^2_j + y^2_{j+1} + 2y_j y_{j+1}\beta_{j,j+1}]^{1/2}$ and:

$$\beta_{j,j+1} = \mathbf{u}_j \mathbf{u}_{j+1} = \cos(\varphi_{j+1} - \varphi_j). \tag{17}$$

Specifically, one supposes [1, 4]:

$$\hbar\omega_{0,l} > \hbar\omega_{0,l,l+1} > K_B T \text{ , } \hbar\omega_{0,l,l+1} > \frac{\hbar^2 A_{ll}}{d^2_l} \tag{18}$$

for any l. This and Subsection 3.1 will characterize a freely-rotating chain: constrained distances between neighbours and next-to-nearest ones. Then:

$$U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j + \sum_{j=1}^{N-2} V^{(2)}_{j,j+1} \tag{19}$$

The $N - 1$ angular variables in φ will be replaced by other more suitable $N - 1$ ones, namely: $\varphi_0 (\equiv (N-1)^{-1}\sum_{i=1}^{N-1}\varphi_l)$ and the set of all $\beta_{j,j+1}$, using (17). Various useful $D = 2$ formulae will be collected in Appendix A. One has: $[\mathbf{d\Omega}]_2 = [\prod_{j=1}^{N-2} d\beta_{j,j+1}] d\varphi_0 J_2$.

The following approximations for suitably large $\omega_{0,j}$ and $\omega_{0,j,j+1}$ will be lead from Eq. (14) to a new model for a $2D$ freely-rotating chain with radial and angular constraints and small vibrations. Let: $\beta^{(0)}_{j,j+1} = (\mathbf{u}_l \mathbf{u}_{l+1})^{(0)} = (2d_j d_{j+1})^{-1}$ $(d^2_{j,j+1} - d^2_j - d^2_{j+1})$. One approximates:

$$\beta_{j,j+1} \simeq \beta^{(0)}_{j,j+1} + b_{j,j+1} \tag{20}$$

($|b_{j,j+1}| \ll |\beta^{(0)}_{j,j+1}|$, in order to allow for small angular variations $|b_{j,j+1}|$ about the constant $|\beta^{(0)}_{j,j+1}|$. Let $b_{nn} = (b_{1,2}, \ldots, b_{N-2,N-1})$. One has: $V^{(2)}_{j,j+1} \to V^{(2)}_{frv,j,j+1} = 2^{-1} B_{j,j+1}\omega^2_{0,j,j+1}(d_j d_{j+1}/d_{j,j+1})^2 b^2_{j,j+1}$. Variables will be changed, by recalling the above transformation: $(x, \varphi) \to (x, \varphi_0, b_{nn})$. Then $\prod_{l=1}^{N-1} d_l dx_l [\mathbf{d\Omega}]_2 \to \prod_{l=1}^{N-1} d_l dx_l [\mathbf{d\Omega}]_{2,fr} J_{2,fr}$, $[\mathbf{d\Omega}]_{2,fr} = d\varphi_0 \prod_{l=1}^{N-2} db_{j,j+1}$. See Appendix A for the Jacobian J_2 and for the (constant) Jacobian $J_{2,fr}$.

The molecular chain with those small radial and angular vibrations is described by stationary wavefunctions $\psi = \psi(x, \varphi_0, b_{nn})$. On physical grounds, wavefunctions take on their dominant contributions for small values of all $b_{j,j+1}$. By allowing for $-\infty < b_{j,j+1} < +\infty$, the contributions of non small values $|b_{j,j+1}|$ will be subdominant. The new global $2D$ scalar product of two wavefunctions ψ_j, $j = 1, 2$: is:

$$(\psi_1,\ \psi_2)_{2,frv} \equiv \int_{-\infty}^{+\infty} \prod_{l=1}^{N-1} d_l dx_l \int_0^{2\pi} \int_{-\infty}^{+\infty} \prod_{l=1}^{N-2} [\mathbf{d\Omega}]_{2,fr} J_{2,fr} \psi_1{}^* \psi_2, \tag{21}$$

In connection to (13), one defines here:

$$\boldsymbol{\pi}_{2,frv,i} = -i\hbar \frac{\partial}{\partial x_i} \mathbf{u}_i + \frac{\mathbf{e}_{2,frv,i}}{d_i} \tag{22}$$

$$\mathbf{e}_{2,frv,i} = \frac{i\hbar \mathbf{u}_l}{\lambda} - i\hbar \mathbf{u}_{\varphi_i} [\frac{1}{N-1} \frac{\partial}{\partial \varphi_0} + a_{i,i+1}^{(0)} \frac{\partial}{\partial b_{i,i+1}} - a_{i-1,i}^{(0)} \frac{\partial}{\partial b_{i-1,i}}] \tag{23}$$

$$\mathbf{e}_{2,frv,r,i} = \frac{i\hbar \mathbf{u}_l}{\lambda} - i\hbar \mathbf{u}_{\varphi_i} \frac{1}{N-1} \frac{\partial}{\partial \varphi_0} \tag{24}$$

$$\boldsymbol{\pi}_{2,frv,v,i} = -i\hbar \frac{\partial}{\partial x_i} \mathbf{u}_i - \frac{i\hbar \mathbf{u}_{\varphi_i}}{d_i} (a_{i,i+1}^{(0)} \frac{\partial}{\partial b_{i,i+1}} - a_{i-1,i}^{(0)} \frac{\partial}{\partial b_{i-1,i}}) \tag{25}$$

with $a_{j,j+1}^{(0)}$ given in Eq. (62), Appendix A. λ is a parameter: $\mathbf{e}_{2,frv,i}$ is Hermitean under Eq. (21) only if $\lambda = 2(N-1)$, to be assumed in what follows. Notice the change of structure between the two expressions for $\mathbf{e}_{2,i}$ (Eq. (11)) and $\mathbf{e}_{2,frv,i}$. By assumption, the approximate 2*D* Hamiltonian describing small vibrations about constrained distances between neighbour and next-to-near neighbours atoms is ($U_{frv}^{(2)} = \sum_{j=1}^{N-2} V_{frv,j,j+1}^{(2)}$) :

$$\tilde{H}_{2,frv}^{(2)} = \frac{1}{2} \sum_{i,j=1}^{N-1} A_{ij} \boldsymbol{\pi}_{2,frv,i} \boldsymbol{\pi}_{2,frv,j} + U_{fjv} + U_{frv}^{(2)} \tag{26}$$

$\boldsymbol{\pi}_{2,frv,i}$ and $\tilde{H}_{2,frv}^{(2)}$ generalize Eqs. (13) and (14). As $\lambda = 2(N-1)$, an important property is the Hermiticity of $\tilde{H}_{2,frv}^{(i)}$ with the 2*D* scalar product (21).

The total orbital angular momentum $L_2 = \sum_{i=1}^{N-1} (-i\hbar)(\partial/\partial\varphi_i) = -i\hbar(\partial/\partial\varphi_0)$ commutes with $\tilde{H}_{2,frv}^{(2)}$. Then, there are common eigenfunctions $\psi_{E,m}$ for $\tilde{H}_{2,frv}^{(2)} \psi_{E,m} = E\psi_{E,m}$ and $L_2 \psi_{E,m} = \hbar m \psi_{E,m}$ with eigenvalues E and $\hbar m$ ($m = 0, \pm 1, \pm 2, \ldots$, as $\psi_{E,m}$ is periodic in φ_0 with period $2\boldsymbol{\pi}$), respectively. One has: $\psi_{E,m} = \exp im\varphi_0 . f_{E,m}$. The eigenfunction $f_{E,m}$ of $\tilde{H}_{2,frv,m}^{(2)}$ (which results from $\tilde{H}_{2,frv}^{(2)}$ with $-i\hbar(\partial/\partial\varphi_0)$ replaced by $\hbar m$), depends on all x_i and all $b_{j.j+1}$ and is independent on φ_0.

An important point is that in $\tilde{H}_{2,frv,m}^{2}$ the *m*-dependent terms are linear in all x_i and all $b_{j.j+1}$. This implies that they will not contribute to the vibrational frequencies (at least, to orders $\omega_{0,i}$ and $\omega_{0,i,i+1}$, although they will to the eigenfunctions), that is, the vibrational frequencies do not depend on the rotational state. The case $N = 3$ in subsection 3.3 will illustrate it. The following contribution from Eq. (26)

$$\tilde{H}_{2,fr,3} = \frac{1}{2} \sum_{i,j=1}^{N-1} A_{ij} \mathbf{e}_{2,frv,r,i} \mathbf{e}_{2,frv,r,j} \tag{27}$$

can be interpreted as the Hamiltonian for the overall rotations of the fr chain without vibrations. See also Appendix F for the case $N = 3$ and Appendix H for further discussion. There are very important approximately planar (2D) chains: among others, the strict closed rings structures corresponding to the carbohydrate ribose (in RNA) and deoxyribose (in DNA) and the nitrogenous bases (derivatives of pyrimidine) cytosine and thymine (in DNA) and uracil (in RNA). The description of those closed rings, omitted here, would require suitable additions of potentials (linking both ends of the chains) to $U_{fjv} + U_{frv}^{(2)}$ in Eq. (26) (or variants there of).

3.3 2D freely-rotating with vibrations: N = 3. Comparison with experimental data for vibrational frequencies

The Schrodinger equation $\tilde{H}_{2,frv}^{(2)}\psi_{E,m} = E\psi_{E,m}$ for case $N = 3$ (with $\lambda = 4$), with $M_1 = M_3$ ($A_{11} = A_{22}$) and $d_i = d$, $\omega_{0,i} = \omega_0$, $i = 1, 2$, will be analyzed in Appendix F and here. Eq. (26) yields:

$$\tilde{H}_{2,frv}^{(2)} = \tilde{H}_{2,frv,1}^{(2)} + \tilde{H}_{2,frv,2} + \tilde{H}_{2,fr,3} \tag{28}$$

Eq. (28) describes a 2D vibrating quantum "rigid body". $\tilde{H}_{2,fr,3}$ (frequency-independent) accounts for rotations in 2D and has generic eigenfunctions exp $im\varphi_0$ with eigenvalues $\frac{(A_{11} + A_{12}\beta_{12}^{(0)})\hbar^2}{2d^2}[\frac{m^2}{2} + \frac{1}{8}]$. $\tilde{H}_{2,frv,1}^{(2)} + \tilde{H}_{2,frv,2}$ leads to two decoupled Hamiltonians: $\tilde{H}_{2,z,m}$ (one displaced harmonic oscillator), giving rise to the frequency ω_z, and $\tilde{H}_{2,Z,b_{1,2}}^{(2)}$ (two coupled harmonic oscillators), yielding two frequencies, namely, $\omega_{Z,b_{1,2},+}$ and $\omega_{Z,b_{1,2},-}$. The frequencies measured experimentally are ω_z, $\omega_{Z,b_{1,2},+}$ and $\omega_{Z,b_{1,2},-}$. By eliminating both ω_0^2 and $\omega_{0,12}^{(0)}$, the resulting equations (29) and (30)) below involve: ω_z, M_1, M_2, $\omega_{Z,b_{1,2},+}$, $\omega_{Z,b_{1,2},-}$ and $\beta_{12}^{(0)}$ ($A_{12}/A_{11} = -[1 + (M_2/M_1)]^{-1}$).

$$\frac{(\frac{\omega_{Z,b_{1,2},+}}{\omega_z})^2 + (\frac{\omega_{Z,b_{1,2},-}}{\omega_z})^2 - \frac{1 + (A_{12}/A_{12})\beta_{12}^{(0)}}{1 - (A_{12}/A_{11})\beta_{12}^{(0)}}}{(\frac{\omega_{Z,b_{1,2},+}}{\omega_z})^2 . (\frac{\omega_{Z,b_{1,2},-}}{\omega_z})^2} = \rho_2 \tag{29}$$

$$\rho_2 = \frac{(1 - (A_{12}/A_{11})\beta_{12}^{(0)})^2(1 + (M_1/M_2))^2}{1 + 2(M_1/M_2)} \tag{30}$$

Approximate numerical analysis of Eqs. (29) and (30) and comparisons to experimental data are carried out for several triatomic molecules. Frecuencies are given in cm^{-1}. Experimental data for vibrational frequencies are taken from [35]. Complementary and interesting information is given in [1, 9, 36-37]. The following results for and consistency between the left- and right-hand-sides (*lhs*, and *rhs*, respectively) of Eq. (29) have been obtained:

Water vapour (H_2O): $\omega_z = 3756$, $\omega_{Z,b_{1,2},+} = 3657$, $\omega_{Z,b_{1,2},-} = 1595$, $\beta_{12}^{(0)} = 0.259$, $M_H/M_O = 0.063$. *lhs* = 0.979, *rhs* = 1.033.

Hydrogen sulfide (SH_2): $\omega_z = 2626$, $\omega_{Z,b_{1,2},+} = 2615$, $\omega_{Z,b_{1,2},-} = 1183$, $\beta_{12}^{(0)} = 0.035$, $M_H/M_S = 0.03$. *lhs* = 0.97, *rhs* = 1.00.

Heavy water (D_2O): $\omega_z = 2788$, $\omega_{Z,b_{1,2},+} = 2671$, $\omega_{Z,b_{1,2},-} = 1178$, $\beta_{12}^{(0)} = 0.259$, $M_D/M_O = 0.133$. *lhs* = 1.058, *rhs* = 1.050.

Sulfur dioxide (SO_2): $\omega_z = 1360$, $\omega_{Z,b_{1,2},+} = 1151$, $\omega_{Z,b_{1,2},-} = 518$, $\beta_{12}^{(0)} = 0.485$, $M_O/M_S = 0.499$. *lhs* = 1.337, *rhs* = 1.516.

4. 3D open linear chains with vibrations

New models for 3*D* freely-jointed and freely-rotating molecular chains with small vibrations will be contructed in this Section, through new approximations.

4.1 *3D freely-jointed with vibrations*

Like for $D = 2$ in Subsection 3.1, let the frequencies $\omega_{0,j}$ be adequately larger than some suitably energy scale (for instance, K_BT) and let $y_j = d_j + x_j$, with some small (radial) variable displacement x_l. Let: $x = (x_1, \ldots, x_{N-1})$. Variables are changed through: $(y_l, \theta_l, \varphi_l) \to (x_l, \theta_l, \varphi_l)$, $l = 1, \ldots, N-1$. Also: $\prod_{l=1}^{N-1} d^3\mathbf{y}_l \to \prod_{l=1}^{N-1} d_l^2 dx_l [\mathbf{d\Omega}]_3$, $\int_0^{+\infty} y_l^2 dy_l \to \int_{-\infty}^{+\infty} d_l^2 dx_l$, $1/y_l \to 1/d_l$, $\partial/\partial y_l \to \partial/\partial x_l$, $V_j \to V_{fjv,j} = (2A_{jj})^{-1}\omega_{0,j}^2 x_j^2$. The molecular chain with those small radial vibrations is described by wavefunctions: $\psi = \psi(x, \theta, \varphi)$. The new global 3*D* scalar product of two wavefunctions ψ_j, $j = 1, 2$ is:

$$(\psi_1, \psi_2)_{3,frv} \equiv \int_{-\infty}^{+\infty} \prod_{l=1}^{N-1} d_l^2 dx_l \int [\mathbf{d\Omega}]_3 \psi_1(x, \theta, \varphi)^* \psi_2(x, \theta, \varphi), \tag{31}$$

also integrating over the whole $N-1$ solid angles. The actual 3*D* counterpart of (22) and the approximate Hamiltonian describing small "radial" vibrations about constrained distances between neighbour atoms along the molecular chain are:

$$\boldsymbol{\pi}_{3,fjv,i} = -i\hbar \frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{3,i}}{d_i} \tag{32}$$

$$\tilde{H}_{3,fjv} = \sum_{i,j=1}^{N-1} \frac{A_{ij}}{2} \boldsymbol{\pi}_{3,fjv,i} \boldsymbol{\pi}_{3,fjv,j} + U_{fjv} \tag{33}$$

with the same expression for U_{fjv} as in Subsection 3.1. $\boldsymbol{\pi}_{3,fjv,i}$ and $\tilde{H}_{3,fjv}$ are Hermitean with the global 3*D* scalar product in Eq. (31). The total orbital angular momentum $\mathbf{L}_3$ is the same as in Section 2 and commutes with $\tilde{H}_{3,fjv}$. The purely 3*D* angular Hamiltonian and the scalar product for the freely jointed molecular chain are:

$$\tilde{H}_{3,fj} = \sum_{i,j=1}^{N-1} \frac{A_{ij}}{2d_i d_j} \mathbf{e}_{3,i} \mathbf{e}_{3,j} \tag{34}$$

$$(\psi_1, \psi_2)_{3,fj} \equiv \int [\mathbf{d\Omega}]_3 \psi_1(\theta, \varphi)^* \psi_2(\theta, \varphi), \tag{35}$$

the integration being carried out over the whole $N-1$ solid angles. The angular motion is described by wavefunctions $\psi = \psi(\theta, \varphi)$, eigenfunctions of the stationary Schrodinger equation, with energy eigenvalues E:

$$\tilde{H}_{3,fj}\psi = E\psi. \tag{36}$$

The $D = 3$ eigenfunctions of (36) with definite angular momentum are treated briefly in Appendix C. The variational test of consistency in Appendices D and E for $D = 2$ can be readily extended to $D = 3$. The result is the same as in Eq. (82), with the same zero-point energy as for $D = 2$, but with the $D = 3$ operator $\tilde{H}_{3,fjv}$ given in Eq. (33). The purely angular motions described by $\tilde{H}_{3,fj}$ will be essential for the understanding of single polymerization of 3*D* fj chains in Section 5.

4.2 *3D freely-rotating chains with vibrations*

The same energy scales, approximations regarding distances between nearest and next-to-nearest neighbour units and potentials as in Subsection 3.2 for 2*D* are also assumed for 3*D*. Eq. (17) is replaced by:

$$\beta_{j,j+1} = \mathbf{u}_j\mathbf{u}_{j+1} = \cos\theta_j\cos\theta_{j+1} + \sin\theta_j\sin\theta_{j+1}\cos(\varphi_{j+1} - \varphi_j). \tag{37}$$

The $2(N - 1)$ angular1 variables in θ and φ will be replaced by the following more suitable ones: $\theta_1, \ldots, \theta_{N-1}$, $\varphi_0(\equiv (N-1)^{-1}\sum_{j=1}^{N-1}\varphi_j)$ and the set of all $\beta_{j,j+1}$, by using Eq. (37). One has: $[\mathbf{d\Omega}]_3 = [\prod_{j=1}^{N-2} d\beta_{j,j+1}]d\varphi_0[d\theta]J_3$, $[d\theta] = \prod_{l=1}^{N-1} d\theta_l]$, the Jacobian J_3 being given in Appendix A.

For suitably large $\omega_{0,j}$ and $\omega_{0,j,j+1}$, the molecular chain becomes a 3*D* freely-rotating one with small vibrations. The approximations for $\beta_{j,j+1}$ and potentials are the same as those for 2*D*. Let $bnn = (b_{1,2}, \ldots, b_{N-2,N-1})$. Variables are changed as: $(x, \theta, \varphi) \to (x, \theta, \varphi_0, b_{nn})$. Then $\prod_{l=1}^{N-1} d_l^2 dx_l[\mathbf{d\Omega}]_3 \to \prod_{l=1}^{N-1} d_l^2 dx_l[\mathbf{d\Omega}]_{3,fr} J_{3,fr}$, $[\mathbf{d\Omega}]_{3,fr} = d\varphi_0[d\theta]$ $[\prod_{l=1}^{N-2} db_{j,j+1}]$, where $J_{3,fr} = J_{3,fr}(\theta)$ is given in Appendix A.

The new global 3*D* scalar product of two wavefunctions $\psi_j = \psi_j(x, \theta, \varphi_0, b_{nn})$, $j = 1, 2$: is:

$$(\psi_1, \psi_2)_{3,frv} \equiv \int_{-\infty}^{+\infty}\prod_{l=1}^{N-1} d_l^2 dx_l \int_0^{2\pi}\int_{-\infty}^{+\infty}\int_0^{\pi}[\mathbf{d\Omega}]_{3,fr}J_{3,fr}\psi_1^*\psi_2, \tag{38}$$

The total orbital angular momentum $\mathbf{L}_3$ is Hermitean under (38). The molecular chain with those small radial and angular vibrations is described by: $\psi = \psi_j(x, \theta, \varphi_0, b_{nn})$. The 3*D* counterparts of Eqs. (22) and (23), are assumed to be, for simplicity:

$$\boldsymbol{\pi}_{3,frv,i} = -i\hbar\frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{3,frv,i}}{d_i} \tag{39}$$

$$\mathbf{e}_{3,frv,i} = i\hbar\mathbf{u}_i - i\hbar\mathbf{u}_{\theta_i}\frac{\partial}{\partial\theta_i} - i\hbar\mathbf{u}_{\varphi_i}[\frac{1}{N-1}\frac{\partial}{\partial\varphi_0} - a_{3,i,i+1}^{(0)}\frac{\partial}{\partial b_{i,i+1}} + a_{3,i-1,i}^{(0)}\frac{\partial}{\partial b_{i-1,i}}] \tag{40}$$

$a_{3,j-1,j}^{(0)}$ being given by Eq. (64) for $\beta_{l,l+1} = (\mathbf{u}_l\mathbf{u}_{l+1})^{(0)}$. One expresses $\frac{\partial}{\partial\theta_i}$ in $\mathbf{e}_{3,frv,i}$ in terms of $\frac{\partial}{\partial\theta_i}|$, which means differentiation for fixed φ_0, all $b_{i,i+1}$ and any θ_j (except θ_i). One differentiates (37) for fixed $\beta_{j,j+1} = \beta_{j,j+1}^{(0)}$ and uses (66). Then, one recasts $\mathbf{e}_{3,frv,i}$ in terms of (φ_0, b_{nn}) and all θ_j, as:

$$\mathbf{e}_{3,frv,i} = \mathbf{e}_{3,frv,r,i} + \mathbf{e}_{3,frv,v,i} \tag{41}$$

$$\mathbf{e}_{3,frv,r,i} = i\hbar\mathbf{u}_i - i\hbar\mathbf{u}_{\theta_i}\frac{\partial}{\partial\theta_i} | -i\hbar\mathbf{u}_{\varphi_i}\frac{1}{N-1}\frac{\partial}{\partial\varphi_0} \tag{42}$$

$$\mathbf{e}_{3,frv,v,i} = -i\hbar(\mathbf{u}_{i-1} - \beta^{(0)}_{i-1,i}\mathbf{u}_i)\frac{\partial}{\partial b_{i-1,i}} - i\hbar(\mathbf{u}_{i+1} - \beta^{(0)}_{i,i+1}\mathbf{u}_i)\frac{\partial}{\partial b_{i,i+1}} \tag{43}$$

All $\mathbf{u}_i$ and $\mathbf{u}_{\varphi_i}$ are taken at fixed β's. Under Eq. (38), $\mathbf{e}_{3,frv,v,i}$ is Hermitean, but neither $\mathbf{e}_{3,frv,r,i}$ nor $\boldsymbol{\pi}_{3,frj,i}$ are. This (although different from the $2D$ case) will suffice and be convenient. The approximate $3D$ Hamiltonian describing small "radial" vibrations about constrained distances between neighbour and next-to-near neighbours atoms along the molecular chain is supposed to be:

$$\tilde{H}^{(2)}_{3,frv} = \frac{1}{2J_{3,fr}}\sum_{i,j=1}^{N-1} A_{ij}\boldsymbol{\pi}^{+}_{3,frv,i}J_{3,fr}\boldsymbol{\pi}_{3,frv,j} + U_{fjv} + U^{(2)}_{frv} \tag{44}$$

$\boldsymbol{\pi}^{+}_{3,frv,i}$ is the operator adjoint of $\boldsymbol{\pi}_{3,frv,i}$, with respect to the scalar product (38). $U_{fjv} + U^{(2)}_{frv}$ are the same as in Eq. (26). $\tilde{H}^{(2)}_{3,frv}$ is Hermitean with the $3D$ scalar product in Eq. (38).

An analisis of $3D$ purely rotational motion is more complicated than for $D = 2$ and, so, it requires an specific analysis. See Subsection 4.3 and Appendixes G and H.

By considering rotational motions only, units $\mathbf{u}_i$ and $\mathbf{u}_j$ in a fr chain tend to be the more uncorrelated the larger $|i - j|$ is: then, the fr chain can be approximated by a fj one formed by effective units (each constituted by a number of units of the previous fr chain) having larger effective lengths d_e [1, 3].

4.3 *3D freely-rotating chain with vibrations: N = 3. Comparison of vibrational motions in 3D and 2D*

The Schrodinger equation $\tilde{H}^{(2)}_{3,frv}\psi_{E,m} = E\psi_{E,m}$ for $N = 3$, with $M_1 = M_3$ ($A_{11} = A_{22}$) and $d_1 = d_2 = d$, $\omega_{0,1} = \omega_{0,2} = \omega_0$ will be analyzed here in outline. Eq. (44) yields:

$$\tilde{H}^{(2)}_{3,frv} = \tilde{H}^{(2)}_{3,frv,1} + \tilde{H}_{3,frv,2} + \tilde{H}_{3,fr,3} \tag{45}$$

$$\tilde{H}^{(2)}_{3,frv,1} = \frac{1}{2}\sum_{i,j=1}^{2} A_{ij}\left(-i\hbar\frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{3,frv,v,i}}{d_i}\right)\left(-i\hbar\frac{\partial}{\partial x_j}\mathbf{u}_j + \frac{\mathbf{e}_{3,frv,v,j}}{d_j}\right) + U_{fjv} + U^{(2)}_{frv} \tag{46}$$

$$\tilde{H}_{3,fr,3} = \frac{1}{2J_{3,fr}}\sum_{i,j=1}^{2} A_{ij}\frac{\mathbf{e}^{+}_{3,frv,r,i}}{d_i}J_{3,fr}\frac{\mathbf{e}_{3,frv,r,j}}{d_j} \tag{47}$$

$\tilde{H}^{(2)}_{3,frv,1}$ has been simplified because $\left(-i\hbar\frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{3,frv,v,i}}{d_i}\right)$ is Hermitean and commutes with $J_{3,fr}$. Eq. (45) describes a $3D$ vibrating quantum "rigid body". By using Eq. (43), and performing scalar products of various $\mathbf{u}_j$ vectors, one shows directly that $\tilde{H}^{(2)}_{3,frv,1} = \tilde{H}^{(2)}_{2,frv,1}$: the $3D$ purely vibrational motion coincides with the $2D$ one, studied in

Subsection 3.3 and Appendix F. Then, the consistency of the $2D$ vibrational frequencies computed in Subsection 3.3 with experimental data continues to hold for the present $3D$ analysis.

$\tilde{H}_{3,frv,2}$ comes from the interference between $(-i\hbar\frac{\partial}{\partial x_i}\mathbf{u}_i+\frac{\mathbf{e}_{3,frv,v,i}}{d_i})s$ and $\frac{\mathbf{e}_{3,frv,r,j}}{d_j}s$. Both $\tilde{H}_{3,frv,2}$ and $\tilde{H}_{3,frv,3}$ differ from their counterparts in $2D$. $\tilde{H}_{3,fr,3}$ is in principle a possible candidate for accounting for $3D$ rotational motion (it may be influenced by contributions from $\tilde{H}_{3,frv,2}$). For further analysis, see Appendixes G and H.

5. 3D polymerization of one single unit in open fj chains: quantum-classical description

5.1 *Formulation of the model*

The preceding approximate quantum descriptions provide a basis for approximate models for $3D$ single polymerization, namely, the growth of a molecular chain (from small to large) formed by units 2, …, N, by binding the additional unit 1. It will be physically equivalent, and certainly more economical (since the overall center-of mass of all units 1, 2, …, N has been factored out), to work with $\mathbf{y}_1$, instead of with $\mathbf{R}_1$. For simplicity, in the present model for polymerization, there is a fluid containing a very dilute solution of chains, the latter being adequately separated, on average, from one another. Consequently, one could proceed to the polymerization process in one single system: one unit and an individual chain (independently from the others).

The system (chain and unit 1) evolves in solution in a fluid at rest, in thermal equilibrium at K_BT adequately smaller than all $\hbar\omega_{0,i}$ and so that, by assumption, all vibrational states are the ground ones and the relevant degrees of freedom of the chain are the rotational ones (say, in principle, those in $\tilde{H}_{3,fj}$). The single unit 1, with kinetic energy in a suitable interval about K_BT, interacts only with unit 2 in the chain through the (at least, partly) attractive and spherically symmetric potential $U_1 = U_1(\mathbf{y}_1) = U_1(y_1)$ $(y_1 = |\mathbf{y}_1|)$: eventually, unit 1 becomes bound to unit 2. Unit 1 will be dealt with quantum-mechanically, as so is its binding process genuinely. For simplicity, no catalyst is considered.

In principle, the dynamics is accounted for by the quantum Wigner function for the chain and unit 1 and the associated non-equilibrium equation [38-40]. However, it is physically adequate, due to the influence of the fluid at such K_BT, to approximate the quantum descriptions of the rotational motions of the fj chain in Subsection 4.1 by that provided by classical statistical mechanics.

For units 2, …, N forming the chain, the approximate transition to classical mechanics reads: $\mathbf{e}_{3,i} \to -\mathbf{a}_{3,c,i}$, $-i\hbar\frac{\partial}{\partial\theta_i} \to \pi_{\theta_i,c}$, $-i\hbar\frac{\partial}{\partial\varphi_i} \to \pi_{\varphi_i,c}$. The terms proportional to $i\hbar\mathbf{u}$ s disappear. $\pi_{\theta_i,c}$, $\pi_{\varphi_i,c}$ are classical momenta, canonically conjugate to θ_i, φ_i. Let $\theta_p = (\theta_2, \ldots, \theta_{N-1})$, $\pi_{\theta,c,p} = (\pi_{\theta_{2,c}}, \ldots, \pi_{\theta_{N-1},c})$, and so on for φ_p, $\pi_{\varphi,c,p}$, omitting unit 1. Let $\boldsymbol{\pi}_{3,c,1}$, be a momentum, canonically conjugate to $\mathbf{y}_1$, for the quantum-mechanical unit 1. From the above comments, the system is described by a mixed (quantum-classical) distribution function in phase-space: a quantum Wigner-like one for unit 1 and a classical Liouville-like one for the chain: $f_m = f_m(\mathbf{y}_1, \theta_p, \varphi_p, \boldsymbol{\pi}_{3,c,1}, \pi_{\theta,c,p}, \pi_{\varphi,c,p}; t)$. By assumption, f_m fulfills the time(t)-reversible mixed (integro-differential) Wigner-Liouville equation:

$$\frac{\partial f_m}{\partial t} = -(A_{11}\boldsymbol{\pi}_{3,c,1} + (A_{21}/d_2)(-\mathbf{a}_{3,c,2}))(\nabla_{\mathbf{y}_1} f_m) + \int d^3\boldsymbol{\pi}_{3,c,1,0} f_m(\boldsymbol{\pi}_{3,c,1,0}) \int \frac{id^3\mathbf{y}_{1,0}}{\hbar(\pi\hbar)^3} \exp[\frac{2i(\boldsymbol{\pi}_{3,c,1}-\boldsymbol{\pi}_{3,c,1,0})\mathbf{y}_{1,0}}{\hbar}]$$

$$\times [U_1(\mathbf{y}_1+\mathbf{y}_{1,0}) - U_1(\mathbf{y}_1-\mathbf{y}_{1,0})] + [\tilde{H}_{3,fj,c,2}, f_m]_{Pb}$$

$$+(A_{12}/d_2)\boldsymbol{\pi}_{3,c,1}[\frac{\partial(-\mathbf{a}_{3,c,2})}{\partial\theta_2}\frac{\partial f_m}{\partial\pi_{\theta_2}} - \frac{\partial(-\mathbf{a}_{3,c,2})}{\partial\pi_{\theta_2}}\frac{\partial f_m}{\partial\theta_2} + \frac{\partial(-\mathbf{a}_{3,c,2})}{\partial\varphi_2}\frac{\partial f_m}{\partial\pi_{\varphi_2}} - \frac{\partial(-\mathbf{a}_{3,c,2})}{\partial\pi_{\varphi_2}}\frac{\partial f_m}{\partial\varphi_2}] \tag{48}$$

with $\tilde{H}_{3,\mathit{fj},c,2} = \sum_{i,j=2}^{N-1} (A_{ij}/2d_i d_j)(-\mathbf{a}_{3,c,i})(-\mathbf{a}_{3,c,j})$. $[\tilde{H}_{3,\mathit{fj},c,2}, f_m]_{Pb}$ denotes the standard classical Poisson bracket [37, 40]. It approximates, in the classical regime, an integral contribution for the chain analogous to the one in Eq. (48) for unit 1. Notice that $A_{12}\boldsymbol{\pi}_{3,c,1}$ is multiplied by the Poisson bracket of $(-\mathbf{a}_{3,c,2})$ and f_m. $f_m(\boldsymbol{\pi}_{3,c,1,0})$ is obtained just by replacing $\boldsymbol{\pi}_{3,c,1}$ by $\boldsymbol{\pi}_{3,c,1,0}$ in f_m. The dynamics will be considered for suffciently long time (t), so that the chain is essentially in thermal equilibrium at T. The solvent at thermal equilibrium is responsible for each individual chain to be also at thermal equilibrium, at the same temperature. Notice that $(-\mathbf{a}_{3,c,2})$ is coupled to $\nabla_{\mathbf{y}_1}$. This influences the dynamics of unit 1 without altering the equilibrium states of the *fj* chain. Let $[\mathbf{d\Omega}]_{3,L} = \prod_{i=2}^{N-1} d\theta_i d\pi_{\theta,c,i} d\varphi_i d\pi_{\varphi,c,i}$. Total probability is conserved, consistently: $\partial \int d^3\mathbf{y}_1 \int d^3\boldsymbol{\pi}_{3,c,1} \int [\mathbf{d\Omega}]_{3,L}\, f_m/\partial t = 0$.

By assumption: i) the chain and its influence on unit 1 are described by the (t-independent) classical Boltzmann equilibrium distribution $f_{eq,2} = Z_{eq,2}^{-1} \exp[-(K_B T)^{-1}[(A_{12}/d_2)\boldsymbol{\pi}_{3,c,1}(-\mathbf{a}_{3,c,2}) + \tilde{H}_{3,\mathit{fj},c,2}]]$ ($Z_{eq,2} = [\mathbf{d\Omega}]_{3,L} \exp[-(K_B T)^{-1} \tilde{H}_{3,\mathit{fj},c,2}]$), which includes $\boldsymbol{\pi}_{3,c,1}(-\mathbf{a}_{3,c,2})$, ii) $f_m \simeq f_1 f_{eq,2}$, with $f_1 = f_1(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1}, t)$, solves approximately Eq. (48). The contribution of $A_{12}\boldsymbol{\pi}_{3,c,1}$ times the Poisson bracket multiplying it plus that of the Poisson bracket ($[\tilde{H}_{3,\mathit{fj},c,2}]_{Pb}$) acting upon f_m give a vanishing result. Then: $\int [\mathbf{d\Omega}]_{3,L}\, f_m \simeq f_1 \int [\mathbf{d\Omega}]_{3,L}\, f_{eq,2}$, and $\int [\mathbf{d\Omega}]_{3,L}\, f_1 f_2 (-\mathbf{a}_{3,c,2}) \simeq f_1 \int [\mathbf{d\Omega}]_{3,L}\, f_{eq,2}(-\mathbf{a}_{3,c,2}) = f_1[-(K_B T d_2)/A_{12})(\nabla_{\boldsymbol{\pi}_{3,c,1}} \int [\mathbf{d\Omega}]_{3,L}\, f_{eq,2}$. $\int [\mathbf{d\Omega}]_{3,L}\, f_{eq,2} \equiv f_2 = f_2(\boldsymbol{\pi}_{3,c,1})$ is studied in Appendix J. Eq. (48) becomes, in terms of $W = W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1}, t) = f_1 f_2$:

$$\frac{\partial W}{\partial t} = -[A_{11}\boldsymbol{\pi}_{3,c,1} - (K_B T)(\nabla_{\boldsymbol{\pi}_{3,c,1}} \ln f_2)](\nabla_{\mathbf{y}_1} W) + \int d^3\boldsymbol{\pi}_{3,c,1,0} W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1,0}, t)]$$

$$\times \int \frac{i d^3\mathbf{y}_{1,0}}{\hbar(\pi\hbar)^3} \exp(\frac{2i(\boldsymbol{\pi}_{3,c,1} - \boldsymbol{\pi}_{3,c,1,0})\mathbf{y}_{1,0}}{\hbar})[U_1(|\mathbf{y}_1 + \mathbf{y}_{1,0}|) - U_1(|\mathbf{y}_1 - \mathbf{y}_{1,0}|)] \tag{49}$$

The (t-reversible) quantum Wigner Eq. (49) depends only on the degrees of freedom of unit 1: the non-trivial $f_2(\boldsymbol{\pi}_{3,c,1})$ embodies the influence of the chain at equilibrium. The structure of $f_2(\boldsymbol{\pi}_{3,c,1})$ is a consequence of the tendency of unit 1 to interact with unit 2 (and not with the other units 3, ..., N), the factoring out of the overall CM of all units 1, 2, ..., N and the fact that all units 2, ..., N constitute a classical *fj* at thermal equilibrium. Eq. (49) is the standard Wigner equation for the non-standard quantum Hamiltonian $\tilde{H}_{n-s,1} = -(\hbar^2/2)(A_{11}\nabla_{\mathbf{y}_1}^2 + [\nabla_{\boldsymbol{\pi}_{3,c,1}} \ln f_2](\boldsymbol{\pi}_{3,c,1} \to -i\hbar\nabla_{\mathbf{y}_1})\nabla_{\mathbf{y}_1} + U_1(|\mathbf{y}_1|)$ for unit 1.

As it is difficult to handle $\tilde{H}_{n-s,1}$, it will be approximated by $\tilde{H}_{\mathit{eff},1}$ below. Accordingly, one approximates: $-(K_B T)(\nabla_{\boldsymbol{\pi}_{3,c,1}} \ln f_2) \simeq A_{12}\sigma\boldsymbol{\pi}_{3,c,1}$: see Appendix J. The constant σ (> 0 and dimensionless) accounts for the influence of the classical fj chain on the dynamics of unit 1. After this approximation, Eq. (49) becomes the following standard Wigner equation:

$$\frac{\partial W}{\partial t} = -(A_{11} + A_{12}\sigma)\boldsymbol{\pi}_{3,c,1}(\nabla_{\mathbf{y}_1} W) + \int d^3\boldsymbol{\pi}_{3,c,1,0} W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1,0}, t)]$$

$$\times \int \frac{i d^3\mathbf{y}_{1,0}}{\hbar(\pi\hbar)^3} \exp(\frac{2i(\boldsymbol{\pi}_{3,c,1} - \boldsymbol{\pi}_{3,c,1,0})\mathbf{y}_{1,0}}{\hbar})[U_1(|\mathbf{y}_1 + \mathbf{y}_{1,0}|) - U_1(|\mathbf{y}_1 - \mathbf{y}_{1,0}|)] \tag{50}$$

for the effective quantum Hamiltonian for unit 1: $\tilde{H}_{\mathit{eff},1} = -(\hbar^2/2)(A_{11} + A_{12}\sigma)\nabla_{\mathbf{y}_1}^2 + U_1(|\mathbf{y}_1|)$, which yields continuum and bound states, associated to unbound motion and polymerization of unit 1, respectively.

5.2 *Long time approximations and irreversible Schmolukowski equation: mean first passage time (MFPT)*

Let: $W_{[0]} = W_{[0]}(\mathbf{y}_1, t) = \int d^3\boldsymbol{\pi}_{3,c,1})W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1}, t)$. For long t, the counterpart of the t-reversible Eq. (49) for $\tilde{H}_{eff,1}$ is transformed into a t-irreversible Schmolukowski one for $W_{[0]}$ in Eqs. (107)-(108), by approximating as in [41] (which introduces T-dependences). See Appendix J. The physically interesting solution is, naturally, spherically symmetric ($W_{[0]} = W_{[0]}(y_1, t)$) so that Eqs. (107)-(108) become:

$$\frac{\partial W_{[0]}}{\partial t} = q_{eq}(A_{11} + A_{12}\sigma)(\frac{\partial}{\partial y_1} + \frac{2}{y_1})(D[-q_{eq}(A_{11} + A_{12}\sigma)\frac{\partial}{\partial y_1}(\epsilon_{[2],[0]}W_{[0]}) + \frac{1}{q_{eq}}\frac{\partial U_1}{\partial y_1}W_{[0]}]) \tag{51}$$

with $q_{eq} = (2K_BT/(A_{11} + A_{12}\sigma))^{1/2}$. The diffusion coefficient $D = D(y_1)$ (> 0) and $\epsilon_{[2],[0]} = \epsilon_{[2],[0]}(y_1)$(< 0) are discussed in Appendix J. It is convenient to replace $W_{[0]}$ by another distribution $f = f(y_1, t) = y_1^{-2}W_{[0]}(y_1, t)$. Eq. (51) becomes:

$$\frac{\partial f}{\partial t} = q_{eq}(A_{11} + A_{12}\sigma)\frac{\partial}{\partial y_1}[D[(-q_{eq}(A_{11} + A_{12}\sigma)\frac{\partial}{\partial y_1}(\epsilon_{[2],[0]}f) + \frac{1}{q_{eq}}\frac{\partial U_1}{\partial y_1}f + \frac{2}{y_1}q_{eq}\epsilon_{[2],[0]}(A_{11} + A_{12}\sigma)f]] \tag{52}$$

which can be treated with various well-documented approximation techniques [12, 42-43], out of which the following one will be selected. It is interesting to compute approximately the time required for unit 1 to become attached to the chain as a next neighbour of unit 2, which implements polymerization. Such a time leads to an approximate estimate for probability of polymerization of unit 1 by the chain [43]. In more technical language, that boils down to study the mean first passage time (MFPT) formalism [12, 42-43], which is useful. The MFPT $t(y_1)$, providing an estimate of that time, is the solution of the so-called adjoint equation associated to Eq. (52):

$$q_{eq}^2(A_{11} + A_{12}\sigma)^2(-\epsilon_{[2],[0]})\frac{\partial}{\partial y_1}[D\frac{\partial t(y_1)}{\partial y_1}] - Dq_{eq}(A_{11} + A_{12}\sigma)(\frac{1}{q_{eq}}\frac{\partial U_1}{\partial y_1} + \frac{2q_{eq}\epsilon_{[2],[0]}(A_{11} + A_{12}\sigma)}{y_1})\frac{\partial t(y_1)}{\partial y_1} = -1 \tag{53}$$

provided that suitable boundary conditions be added. It is supposed that $U_1(y_1)$: i) is finite for $0 < y_1 < +\infty$, ii) is > 0 for $0 < y_1 < y_{1,0}$ (repulsive), iii) vanishes very quickly for $y_1 > y_{1,1}$, iv) is < 0 (attractive) in $y_{1,0} < y_1 < y_{1,1}$, v) has a minimum at $y_1 = y_{1,min}$, $y_{1,0} < y_{1,min} < y_{1,1}$, vi) $(\partial U_1/\partial y1) > 0$ in $y_{1,min} < y_1$. That is, $U_1(y_1)$ is qualitatively similar to a Morse-like potential. The natural boundary conditions for polymerization are chosen to be: $t(y_{1,ab}) = 0$ (absorption), with $y_{1,min} < y_{1,ab} < y_{1,1}$ and $[\partial t(y_1)/\partial y_1]_{y_1 = y_{1,2}} = 0$, with $y_{1,1} < y_{1,2}$ (reflection). Then, by a direct integration following [12, 42-43], the solution of Eq. (53) with those boundary conditions is:

$$t(y_1) = \int_{y_{1,ab}}^{y_1} \frac{ds_1}{D(s_1)s_1^2(q_{eq}(A_{11} + A_{12}\sigma))^2}J(s_1) \tag{54}$$

$$J(s_1) = \int_{s_1}^{y_{1,2}} \frac{ds_2 s_2^2}{(-\epsilon_{[2],[0]}(s_2))}\exp[\frac{1}{2K_BT}\int_{s_1}^{s_2}\frac{ds_3(\partial U_1/\partial s_3)}{\epsilon_{[2],[0]}(s_3)}] \tag{55}$$

Let y_1 lie in $y_{1,ab} < y_1 \ll y_{1,2}$ far from $y_{1,2}$. Then, $\int_{s_1}^{s_2}\frac{ds_3(\partial U_1/\partial s_3)}{\epsilon_{[2],[0]}(s_3)} < 0$, as $\epsilon_{[2],[0]}(s_3) < 0$. The latter also implies that $J(s_1) > 0$. That yields a T dependence in the right direction to provide a qualitative agreement with the well known

Arrhenius exponential formula for rate constants and with the fact that as T decreases, so does $t(y_1)$: unit 1 requires a shorter time to reach the close proximity of unit 2. To proceed one step further, one may argue that the dominant approximation to the last integral, due to the properties of $\epsilon_{[2],[0]}$ (Appendix J) and $(\partial U_1/\partial y1)$, comes the lowest integration limit (s_1) and is: $U_1(s_1)/(-\epsilon_{[2],[0]}(s_1))$. Then,

$$t(y_1) \simeq [\int_{y_{1,ab}}^{y_1} \frac{ds_1}{D(s_1)s_1^2(q_{eq}(A_{11}+A_{12}\sigma))^2} \exp[\frac{U_1(s_1)}{2K_BT(-\epsilon_{[2],[0]}(s_1))}].[\int_{s_1}^{y_{1,2}} \frac{ds_2 s_2^2}{(-\epsilon_{[2],[0]}(s_2))}] \tag{56}$$

which displays somewhat better such a T-dependence and, equivalently, that as $|U_1(s_1)|$ increases (with $U_1(s_1) < 0$) unit 1 requires a shorter time to become bound to unit 2. Still further approximations in the integral over s_1 in Eq. (56) could be done, but they will be omitted. $t(y_1)^{-1}$ can be interpreted, approximately as the rate for polymerization. It follows that $t(y_1)^{-1}$ is given by integrals containing exponentials with a T dependence and the correct sign ressembling the well known Arrhenius exponential formula for rate constants in chemical reactions [2-3]. Further study about this lies outside the scope of this work.

6. Conclusions and discussion

6.1 *Conclusions*

The main results in this work have a dual character:

a) Previous works on quantized constrained molecular chains [27-31] led to models for rotational degrees of freedom in the latter. However, it was difficult to include small vibrations in the resulting quantum Hamiltonians in [27-31]. One novelty of the present work is that through simple (but non-trivial) modifications of those models, new Hamiltonians can be constructed which include small vibrations.

a1) A systematic quantum-mechanical approach to 2*D* and 3*D* molecular chains with small vibrations about *fj*, *fr* and torsional constraints, based upon vector operators (generically denoted as **e**) associated to units and the search for Hermitean Hamiltonians, is developed thereby reformulating standard procedures based upon cartesian coordinates and zero modes. Hermiticity of the **e**'s does not hold in all cases: for instance, a Hermitean $\mathbf{e}_{2,frv,i}$ is used for $D = 2$, but non-Hermitean $\mathbf{e}_{2,frv,i}$ is employed for $D = 3$. However, the crucial Hermiticity of the corresponding Hamiltonian always holds.

a2) Systematic consistency checks of the present approach are presented. In particular, the vibrational frequencies of certain triatomic molecules studied in subsection 3.3 are physically consistent with those already obtained through standard approaches [36] (see also [9, 37]). That can be regarded as an encouraging $D = 2$ check of consistency of the present vector formulation. The possibility of applying the quantum Hamiltonians presented in this work to study small vibrations of other small molecular chains is open: for instance, to closed-ring $D = 2$ chains (provided that suitable potentials be assumed).

b) A new quantum-mechanical analysis of 3*D* single polymerization by a molecular chain is presented, namely, about the growth of a fj chain formed by units 2, …, N, by binding the additional unit 1 (in the absence of a catalyst, for simplicity). The system (chain and unit 1) evolves in solution in a fluid at rest, in thermal equilibrium at K_BT such that, by assumption, all vibrational states of the chain are the ground ones and only $\tilde{H}_{3,fj}$ (Eq. (34) matters. The fj chain is assumed to be in thermal equilibrium in the fluid (and, so, approximately described by the Boltzmann distribution), while unit 1 is not. The starting point is a mixed (quantum-classical) distribution function in phase-space (Eq. (48)): a quantum Wigner-like one for unit 1 and a classical Liouville one for the chain. It leads to a quantum Wigner equation for unit 1 alone (Eq. (49)), for a non-standard Hamiltonian due to the influence of the fj chain. Further approximations yield a quantum Wigner equation for unit 1 alone (Eq. (50)), now for a standard Hamiltonian. The latter, in turn, is subject to other approximations which implement the irreversibility inherent to the polymerization process. That leads to an approximate T-dependent Schmolukowski equation (Eq. (51)), also depending on a constant σ (accounting for the influence of the fj chain), a diffusion coefficient D and a dimensionless function $\epsilon_{[2],[0]}$ (associated to both unbound motion of unit 1 and its bound states to unit 2 in the chain).

That Schmolukowski equation enables to derive an explicit formula for the mean first passage time (MFPT) for unit 1 to bind to unit 2 in the chain (Eqs. (54)-(55)) and, hence, an approximate rate for polymerization. The latter displays a temperature dependence resembling the well known Arrhenius exponential formula for rate constants in chemical reaction [2-3], which accounts for the dependence of rate constants in chemical reactions on temperature. This constitutes an, at least qualitative, check of consistency of the present quantum-mechanical approach to polymerization. Further study lies outside this work.

6.2 *Discussion*

A variety of quantum operator variables and Hamiltonians for 2*D* and 3*D* molecular chains have been analyzed in Sections 3,4 and various Appendixes (in particular, K and L). So, it seemed adequate to offer a panoramic overview of various reformulated models of molecular chain with constraints of increasing complexity, through related mathematical techniques. On the other hand, applications to dynamical processes, like polymerization, are more difficult by themselves and the analysis has been restricted to 3*D* fj chains (Section 5).

Having in mind the quantum models [27-31], leading to models for rotational degrees of freedom, a natural question arises: how do they compare with the restrictions of the models presented in the present work for rotational degrees of freedom? Appendices D through I precisely study, through various computations that consistency. In short: i) for freely-jointed chains, in $D = 2$ and $D = 3$, the same models are obtained in [27-31] and here, ii) for freely-rotating chains in $D = 2$, the same conclusion in i) holds (except, possibly, for some constant energy shift of order $\hbar^2(mass \times (bond - length))^{-1}$), iii) for freely rotating chains in $D = 3$, the question is more difficult: see the comment at the end of subsection 4.3 and Appendices G and H. It appears that there may exist more than one consistent quantum Hamiltonian to describe purely the rotations for freely rotating chains in $D = 3$. They appear to be consistent with rotational invariance, have somewhat different structures and would differ by terms of order $\hbar^2(mass \times (bond - length))^{-1}$. See Appendix I. The issue would deserve further study, which lies outside the scope here.

The study of molecular chains also poses conceptual issues. For a system formed by a small molecule, its wave function describes a set of identically prepared independent copies of the system, according to the standard probabilistic interpretation in Quantum Mechanics (see chapter 9 in [44]). On the other extreme, a very large macromolecular chain behaves as a single individual system, described classically: recall single DNA molecule experiments studying the mechanical separation of the two strands (DNA unzipping experiments): see [45] and additional references in [11]. Then, molecular chains, as their length and mass increase, enable to interpolate conceptually from the quantum regime to the classical one: in particular, one could entertain the possibility that the quantum-mechanical wave function would represent consistently one single individual chain, without need of identically prepared copies.

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Conflict of interest

The author declares no conflicts of interest.

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Appendix

A useful definitions, Peierls inequality and various formulae

In order to avoid duplications and save space, the following useful formulae will be referred to along the work.

The scalar product of two complex wavefunctions $\psi_j = \psi_j(u_1, \ldots, u_r)$, depending of spatial variables $u_1, \ldots, u_r$, is:

$$(\psi_1, \psi_2) = \int du_1 ... du_r J(u_1, ..., u_r) \psi_1(u_1, ..., u_r)^* \psi_2(u_1, ..., u_r) \tag{57}$$

$J(u_1, \ldots, u_r)$ being a given non-negative function. The operator adjoint A^+ of the operator A is defined to fulfill:

$$(\psi_1,\ A^+\psi_2) = (A\psi_1,\ \psi_2) \tag{58}$$

for any ψ_j, $j = 1, 2$. Partial integrations and complex conjugation are carried out in relating the rhs and lhs in (58). The operator A is Hermitean if $A^+ = A$.

The following (Peierls) inequality [46] will be employed. Let a quantum system, with Hamiltonian $\tilde{H}$, scalar product (,) and complete set of orthonormal eigenfunctions Ψ_σ (σ being a set of indices), be at thermal equilibrium at absolute temperature T. Then, the equilibrium partition function is: $Z = \Sigma_\sigma (\Psi_\sigma,\ \exp[-(K_B T)^{-1} \tilde{H}] \Psi_\sigma) = \mathrm{Tr}[\exp[-(K_B T)^{-1} \tilde{H}]]$, summing over all possible σ and Tr being the trace. Let Φ_{σ_1} be an arbitrary orthonormal set of wave functions for the system, as the indices in σ_1 vary. It is not required that the set of all Φ_{σ_1} coincide with the complete set of exact eigenfunctions Ψ_σ of $\tilde{H}$. Then, the above Z satisfies Peierls variational inequality [46]:

$$Z \geq \sum_{\sigma_1} \exp[-(K_B T)^{-1} (\Phi_{\sigma_1},\ \tilde{H} \Phi_{\sigma_1})] \tag{59}$$

where the equality holds if the Φ_{σ_1}s are the complete set of exact eigenfunctions Ψ_σ nof $\tilde{H}$. By suitable choices of the Φ_{σ_1}'s, the inequality leads to effective variational Hamiltonians (depending on a smaller set of variables), potentially useful in various dynamical settings. Use of Peierls variational inequality has been made in [28-29, 31].

$D = 2$. The Jacobian J_2 (Subsection 3.2) is:

$$J_2 = J_2[\beta_{1,2} .., \beta_{N-2,N-1}] = [\prod_{l=1}^{N-2} \frac{1}{a_{j,j+1}}], a_{j,j+1} = [1 - \beta_{j,j+1}^2]^{1/2} \tag{60}$$

where Eq. (17) relates $\mathbf{u}_l \mathbf{u}_{l+1}$ to $|\mathbf{y}_l + \mathbf{y}_{l+1}|$. One has:

$$\frac{\partial}{\partial \varphi_j} = \frac{1}{N-1} \frac{\partial}{\partial \varphi_0} - a_{j,j+1} \frac{\partial}{\partial \beta_{j,j+1}} + a_{j-1,j} \frac{\partial}{\partial \beta_{j-1,j}} \tag{61}$$

All partial derivatives are carried out for fixed y_j, for any j. Also: $\frac{\partial}{\partial \beta_{j,j+1}} \to \frac{\partial}{\partial b_{j,j+1}}$ (Subsection 3.2). One has (Subsection 3.2):

$$J_{2,fr} = J_{2,fr}[\beta_{1,2}^{(0)}, .., \beta_{N-2,N-1}^{(0)}],\ a_{j,j+1}^{(0)} = [1 - (\beta_{j,j+1}^{(0)})^2]^{1/2} \tag{62}$$

$D = 3$. The Jacobian J_3 (Subsection 4.2) is:

$$J_3 = J_3[\theta;\beta_{1,2}...\beta_{N-2,N-1}] = [\prod_{l=1}^{N-1}\sin\theta_l][\prod_{l=1}^{N-2}\frac{1}{a_{3,l,l+1}(\beta_{l,l+1})} \tag{63}$$

$$a_{3,l,l+1}(\beta_{l,l+1}) = [(\sin\theta_l\sin\theta_{l+1})^2 - (\mathbf{u}_l\mathbf{u}_{l+1} - \cos\theta_l\cos\theta_{l+1})^2]^{1/2} \tag{64}$$

The relationship of $\mathbf{u}_l\mathbf{u}_{l+1}$ to $|\mathbf{y}_l + \mathbf{y}_{l+1}|$ for $D = 2$ also holds for $D = 3$.

The Jacobian $J_{3,fr}$ (Subsection 4.2) is:

$$J_{3,fr} = J_{3,fr}[\theta] = [\prod_{l=1}^{N-1}\sin\theta_l][\prod_{l=1}^{N-2}\frac{1}{a_{3,l,l+1}(\beta_{l,l+1}^{(0)})} \tag{65}$$

Let $\mathbf{u}_i^+$ be the $3D$ column adjoint to the row vector $\mathbf{u}_i$ and so on for the column vectors $\mathbf{u}_{\theta_i}^+$ and $\mathbf{u}_{\varphi_i}^+$. Then, one has the $3D$ completeness (diadic) relationship:

$$\mathbf{u}_i^+\mathbf{u}_i + \mathbf{u}_{\theta_i}^+\mathbf{u}_{\theta_i} + \mathbf{u}_{\varphi_i}^+\mathbf{u}_{\varphi_i} = I_3 \tag{66}$$

I_3 being the unit 3 × 3 matrix.

B *Angular motion for D = 2 freely-jointed chains: solving Eq. $\tilde{H}_{2,fj}\psi = E\psi$*

It is adequate to have a feeling of the eigenfunctions fulfilling $\tilde{H}_{2,fj}\psi = E\psi$. Then, Eq. (36) will be solved for $N = 3$, $M_1 = M_3$ and $d_i = d$, $i = 1, 2$,. Let: $\varphi_0 = 2^{-1}(\varphi_1 + \varphi_2)$, $\varphi = \varphi_2 - \varphi_1$. One searches for the common eigenfunctions $f = \exp(im\varphi_0)g(\varphi)$ of $L_2 = -i\hbar(\partial/\partial\varphi_0)$ and $\tilde{H}_{2,fj}$, with eigenvalues $m(= 0, \pm1, \pm2, \dots)$ and E, respectively. One gets, with $(d^2/A_{11}\hbar^2)E - 2^{-1}(m^2 + 1) = e_m$ $(0 \le \varphi \le 2\boldsymbol{\pi})$:

$$[-(1-(A_{12}/A_{11}))\cos\varphi)\frac{d^2}{d\varphi^2} - (A_{12}/A_{11})\sin\varphi\frac{d}{d\varphi} - (A_{12}/4A_{11})(1-m^2)\cos\varphi]g = e_m g. \tag{67}$$

It will suffice to search for g as a cosine Fourier series:

$$g(\varphi) = \frac{a_0}{2} + \sum_{n=1}^{+\infty} a_n\cos n\varphi. \tag{68}$$

Upon replacing g in Eq. (67), one gets the three-term infinite recurrence relation for the amplitudes a_n, $n = 1, 2, \dots$

$$A_{+,n+1}a_{n+1} + A_{-,n-1}a_{n-1} = (e_m - n^2)a_n \tag{69}$$

$$A_{+,n+1} = -(A_{12}/2A_{11})(n+1)^2 + (A_{12}/2A_{11})(n+1) + (A_{12}/8A_{11})(1-m^2) \tag{70}$$

$$A_{-,n-1} = -(A_{12}/2A_{11})(n-1)^2 - (A_{12}/2A_{11})(n-1) + (A_{12}/8A_{11})(1-m^2) \tag{71}$$

One drops the a_{n+1}-term in Eq. (67), solves for a_n in terms of a_{n-1} and iterates indefinitely. Then, Eq. (69) for $n = 1, 2, \ldots$ yields:

$$a_n = D_n a_{n-1},\ D_n = \frac{A_{-,n-1}}{e_m - n^2 - A_{+,n+1} D_{n+1} A_{-,n}},\ n = 1, 2, 3, \ldots \tag{72}$$

The successive iterations of Eq. (72) yield D_n, $n = 1, 2, 3, \ldots$, as an infinite continued fraction. For $n = 0$, one also has: $(2(M_2 A_{11})(1 - m^2)a_1 = 4e_{rot,m} a_0$. Combining this and the first equation in (72) for $n = 1$ gives:

$$(A_{12}/8A_{11})(1-m^2)D_1 = e_m. \tag{73}$$

Notice that the infinite continued fraction D_1 depends on e_m, so that Eq. (73) is the eigenvalue equation, that is, an implicit equation for e_m, to be dealt through approximation techniques. For $n \geq n_0$, n_0 being large and fixed, one finds easily the leading approximation $|D_n| \simeq |A_{12}/2A_{11}| \leq 1$. Then, the continued fractions D_n converge, since they fulfill the convergence condition imposed by the Worpitzky theorem [47]. Then, the leading contribution to $\sum_{n=n_0}^{+\infty} a_n \cos n\varphi$ an is bounded by $|a_{n_0}| \sum_{n=n_0}^{+\infty} (|A_{12}/2A_{11}|)^{n-n_0} |\cos n\varphi|$. The last series is (absolutely) convergent and then so is the one giving g in Eq. (68).

C Angular motion for D = 3 freely-jointed chains: solving Eq. (36)

The eigenfunctions fulfilling $\tilde{H}_{3,fj}\psi = E\psi$ for $N = 3$ require much more work than those of $\tilde{H}_{2,fj}\psi = E\psi$ ($N = 2$). That fact will be illustrated with the following study, for $N = 3$. $H_{3,fj}$ commutes with the total orbital angular momentum $\mathbf{L}_3 = \sum_{i=1}^{2} \mathbf{l}_i$ (see Section 2). The problem of finding the common eigenfunctions of $H_{3,fj}$, $\mathbf{L}_3^2$ and the third component $L_{3,z}$ of $\mathbf{L}$ will be treated briefly. The common eigenfunctions of $\mathbf{L}_3^2$ and $L_{3,z}$ are directly provided by the general quantum-mechanical recipes for composing two angular momenta [4]. Let $Y_{l_i}^{m_i} = Y_{l_i}^{m_i}(\theta_i, \varphi_i)$, $i = 1, 2$, be the standard spherical harmonics, which are common eigenfunctions of $\mathbf{l}_i^2$ and the third component $l_{i,z}$ of $\mathbf{l}_i$ with eigenvalues $\hbar^2 l_i(l_i + 1)$ and $\hbar m_i$, respectively [48]. Then the common eigenfunction of $\mathbf{L}_3^2$ and $L_{3,z}$ with eigenvalues $\hbar^2 l(l + 1)$ and $\hbar m$, respectively, are:

$$Y_{l_1,l_2;l}^{m} = \sum_{m_1,m_2} < l_1, l_2;\ m_1, m_2 \,|\, l, m > Y_{l_1}^{m_1} Y_{l_2}^{m_2} \tag{74}$$

with $|l_1 - l_2| \leq l \leq l_1 + l_2$ and the summation is carried out over all m_1, m_2 such that $m_1 + m_2 = m$. The coefficients $< l_1, l_2;$ $m_1, m_2 \,|\, l, m >$ are the so-called Clebsch-Gordan ones [4]. By generalizing the procedure in Appendix B for $D = 2$, the common eigenfunctions $f(E, l.m) = f(E, l.m;\ \theta_1, \varphi_1 \theta_2, \varphi_2)$ of $H_{3,fj}$, $\mathbf{L}_3^2$ and $L_{3,z}$ with eigenvalues E, $\hbar^2 l(l + 1)$ and $\hbar m$, respectively, are searched for as the infinite superpositions:

$$f(E, l.m) = \sum_{l_1,l_2} a(l_1, l_2)_{l,m} Y_{l_1,l_2;l}^{m} \tag{75}$$

with unknown complex (angle-independent) amplitudes $a(l_1, l_2)_{l,m}$, which in principle are allowed to depend on l, m. The summations are carried out, in principle, over all l_1, l_2 compatible with $|l_1 - l_2| \leq l \leq l_1 + l_2$. One has, for any l_1, l_2 with the above restriction for given l:

$$H_{3,fj}Y^{m}_{l_1,l_2;l} = \sum_{l_3,l_4} a_1(l_1, l_2; l_3, l_4)_{l,m}Y^{m}_{l_3,l_4,l} \tag{76}$$

with coefficients $a_1(l_1, l_2; l_3, l_4; l.m)$. One has: $\mathbf{e}_i^2 = \mathbf{l}_i^2 + \hbar^2$ [31] and, by virtue of the action of $\mathbf{e}_i\mathbf{e}_n$, $l \neq n$, the summation in Eq. (76) is limited to $|l_1 - l_3| \leq 1$ and $|l_2 - l_4| \leq 1$. By using Eq. (76) in $H_{3,fj}f(E, l.m) = Ef(E, l.m)$, one gets the following infinite system for all $a(l_1, l_2)_{l,m}$ (for any l_1, l_2 with the above restriction for given l):

$$\sum_{l_1,l_2} a_1(l_1, l_2; l_3, l_4)_{l,m}a(l_1, l_2)_{l,m} = E.a(l_3, l_4)_{l,m} \tag{77}$$

The summations are carried out, in principle, over all l_1, l_2 compatible with $|l_1 - l_3| \leq 1$, $|l_2 - l_4| \leq 1$. The case $M_1 = M_3$, $d_i = d$, $i = 1, 2$, $l = 0$ and $m = 0$ will be treated in outline. By using Eq. (76) and [48], one sees easily that $l_1 = l_2$ and:

$$Y^{0}_{l_1,l_1;0} = C_{l_1}P_{l_1}(\beta_{12}),\ C_{l_1} = \frac{(-1)^{l_1}(2l_1+1)^{1/2}}{4\pi} \tag{78}$$

β_{12} being given in Eq. (17) and P_{l_1} being the Legendre polynomial of order l_1. A direct, but lengthy, computation yields the three-term infinite recurrence relation for the amplitudes $a(l_1, l_1)_{0,0}$, $l_1 = 1, 2, \ldots$

$$B_{+,l_1+1}a(l_1+1, l_1+1)_{0,0} + B_{-,l_1-1}a(l_1-1, l_1-1)_{0,0} = [\frac{Ed^2}{A_{11}\hbar^2} - ((l_1+1)l_1+1)]a(l_1, l_1)_{0,0} \tag{79}$$

$$B_{+,l_1+1} = -(A_{12}/2A_{11})\frac{C_{l_1+1}}{C_{l_1}}(\frac{2(1+(l_1+1)^2)}{2(l_1+1)+1}(l_1+1) + 2(l_1+1)) \tag{80}$$

$$B_{-,l_1-1} = -(A_{12}/2A_{11})\frac{C_{l_1-1}}{C_{l_1}}\frac{2(1+(l_1-1)^2)}{2(l_1-1)+1}l_1 \tag{81}$$

The behaviours of $B_{\pm,l_1}$ for large l1 are similar to those of $A_{\pm,n}$ (Eqs. (70)-(71)) for large n. Then, the analysis of Eq. (79) is essentially similar to that for Eq. (69) and will be omitted.

D *2D and 3D freely-jointed chains with vibrations: consistency of models in Sections 3.1 and 4.1*

The consistency of the new $2D$ and $3D$ freely-jointed models in subsections 3.1 and 3.2 for $\hbar\omega_{0,i} > K_BT$ (only vibrational ground states being relevant) will be outlined here. For that purpose for $2D$, a variational computation inspired on Peierls inequality (Eq. (59) will be performed, by choosing Φ_{σ_1} (normalized with Eq. (12)), as $\Phi_{\sigma_1} = \phi_{gs}(x)$ $f(\varphi)$, $\phi_{gs}(x) = \prod_{i=1}^{2}\phi_{gs,i}$, $\phi_{gs,i}(x_i) = [\omega_{o,i}/A_{ii}\pi\hbar]^{1/4}\exp[-(\omega_{o,i}/2A_{ii}\hbar)x_i^2]$, with $\int_{-\infty}^{+\infty} d_l dx_l \phi_{gs,i}(x_i)^2 = 1$ and $\int[\mathbf{d\Omega}]_2 f^* f = 1$. One has:

$$\int_{-\infty}^{+\infty}\prod_{i=1}^{2} d_l dx_l \phi_{gs}(x)\tilde{H}_{2,fjv}\phi_{gs}(x) = E_{0,v} + \sum_{i,j=1}^{N-1}\frac{A_{ij}}{2d_i d_j}\mathbf{e}_{2,i}\mathbf{e}_{2,j} \tag{82}$$

$$E_{0,v} = E_{0,v,1} + E_{0,v,2}, E_{0,v,1} = \int_{-\infty}^{+\infty} \prod_{i=1}^{2} d_l dx_l \phi_{gs}(x) U_{fjv} \phi_{gs}(x) \tag{83}$$

$$E_{0,v,2} = \int_{-\infty}^{+\infty} \prod_{i=1}^{2} d_l dx_l \phi_{gs}(x) \frac{1}{2} \sum_{i,j=1}^{N-1} A_{ij} [-i\hbar \frac{\partial}{\partial x_i} \mathbf{u}_i] \times [-i\hbar \frac{\partial}{\partial x_j} \mathbf{u}_j] \phi_{gs}(x) \tag{84}$$

Notice that no integration over angles, with $\int[\mathbf{d\Omega}]_2$, is carried out. Crossed integrands of the type $\phi_{gs}(x)\mathbf{e}_i$ $[-i\hbar \frac{\partial}{\partial x_j} \mathbf{u}_j] \phi_{gs}(x)$ for any i and j in the integrations $\int_{-\infty}^{+\infty} \prod_{i=1}^{2} d_l dx_l$, have given vanishing results, by symmetric integrations. The same holds for the contributions in Eq. (84) for $i \neq j$. Gaussian integrations yield: $E_{0,v,1} = E_{0,v,2} = \sum_{i=1}^{N-1} \hbar\omega_{0,i}/4$. Thus, Eq. (82) equals the total zero-point energy ($E_{0,v} = \sum_{i=1}^{N-1} \hbar\omega_{0,i}/2$) (the largest contribution) plus $\sum_{i=1,j}^{N-1} \frac{A_{ij}}{2d_i d_j} \mathbf{e}_{2,i} \mathbf{e}_{2,j}$ (the smaller one, of order $\hbar^2/d^2$ divided by an average atomic mass). This establishes the consistency of Subsection 3.1. The consistency of the new 3*D* model in Subsection 4.1 is similar and will be omitted.

E *Comparison with other models for freely-jointed chains: 3D and 2D*

Different computations [29, 31], using Peierls variational inequality (Eq. (59)) and without employing the approximations in Subsection 4.1, have been carried out based directly in $\tilde{H}$ in Eq. (1) (with $U(\mathbf{y}) = \sum_{i=1}^{N-1} V_j$, $V_j = (2A_{jj})^{-1} \omega_{0,j}^2 (y_j - d_j)^2$) and with $\Phi_{\sigma_1} = \phi_{nn}(y)\psi$, $\phi_{nn}(y) = \prod_{l=1}^{N-1} \phi_l$, $\phi_l = d_l^{-1} [\frac{\omega_{0,l}}{\pi\hbar A_{ll}}]^{1/4} \exp[-\frac{\omega_{0,l}}{2\hbar A_{ll}} (y_l - d_l)^2]$ and $\psi = \psi(\theta, \varphi)$ being a generic complex wavefunction. The analysis, as all $\omega_{0,j}$ are larger than $K_B T$, has led to $(\psi, (\tilde{H}_{3,fj} + E_{0,v})\psi)_{3,fj}$. $\tilde{H}_{3,fj}$ and $E_{o,v}$ are, respectively, the approximate (freely-jointed) Hamiltonian with constrained distances between neighbour atoms along the molecular chain given in (34) and the upper bound for the ground state energy of $\tilde{H}$ appearing in (83): $E_{0,v} = \frac{1}{2} \sum_{i=1}^{N-1} \hbar\omega_{0,j}$. The counterpart of the 3*D* developments just summarized also hold for 2*D*, with the corresponding replacements.

F *2D freely-rotating chain with vibrations: $N = 3$, $M_1 = M_3$, $d_1 = d_2 = d$, $\omega_{0,1} = \omega_{0,2} = \omega_0$*

Several formulae for triatomic molecules, omitted from Subsection 3.3, will be given in this Appendix. Eq. (28), recalling Eq. (26), yields:

$$\tilde{H}_{2,frv,1}^{(2)} = \sum_{i,j=1}^{2} \frac{A_{ij}}{2} \boldsymbol{\pi}_{2,frv,v,i} \boldsymbol{\pi}_{2,frv,v,j} + U_{fjv} + U_{frv}^{(2)} = \frac{A_{11}\hbar^2}{2} [-\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2} - \frac{2(a_{1,2}^{(0)})^2}{d^2} \frac{\partial^2}{\partial b_{1,2}^2}]$$

$$+ \frac{2A_{12}\hbar^2}{2} [-\beta_{12}^{(0)} \frac{\partial^2}{\partial x_1 \partial x_2} + \frac{2\beta_{12}^{(0)} (a_{1,2}^{(0)})^2}{d^2} \frac{\partial^2}{\partial b_{1,2}^2} - \frac{2(a_{1,2}^{(0)})^2}{d} \frac{\partial}{\partial b_{1,2}} (\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2})] + U_{fjv} + U_{frv}^{(2)} \tag{85}$$

$$\tilde{H}_{2,frv,2} = \frac{A_{12} 2\hbar^2 a_{12}^{(0)}}{2d} [\frac{\partial}{\partial x_1} \frac{\partial}{\partial \varphi_0} - \frac{\partial}{\partial x_2} \frac{\partial}{\partial \varphi_0}] \tag{86}$$

$$\tilde{H}_{2,fr,3}=\frac{1}{2}\sum_{i,j=1}^{2}A_{ij}\mathbf{e}_{2,frv,r,i}\mathbf{e}_{2,frv,r,j}=\frac{A_{11}\hbar^2}{2d^2}[-\frac{1}{2}\frac{\partial^2}{\partial\varphi_0^2}+\frac{1}{8}]+\frac{A_{12}\beta_{12}^{(0)}\hbar^2}{2d^2}[-\frac{1}{2}\frac{\partial}{\partial\varphi_0^2}+\frac{1}{8}] \quad (87)$$

Let $\psi_{E,m}$ = exp $im\varphi_0 . f_{E,m}$. Then, $\tilde{H}_{2,fr,3}$ (describing $2D$ rotations) decouples from $\tilde{H}^{(2)}_{2,frv,1}+\tilde{H}_{2,frv,2}$ which, in turn, describes three coupled harmonic oscillators and becomes, by using $x_1 = Z-(z/2)$, $x_2 = Z+(z/2)$, $B_{12} = M_1/2$:

$$\tilde{H}^{(2)}_{2,frv,1}+\frac{A_{12}2\hbar^2 a_{12}^{(0)}im}{2d}[\frac{\partial}{\partial x_1}-\frac{\partial}{\partial x_2}]=\tilde{H}_{2,z,m}+\tilde{H}^{(2)}_{2,Z,b_{1,2}}$$

$$\tilde{H}_{2,z,m}=\frac{(-2A_{11}+2A_{12}\beta_{12}^{(0)})\hbar^2}{2}\frac{\partial^2}{\partial z^2}-\frac{A_{12}2\hbar^2 a_{12}^{(0)}im}{2d}\frac{\partial}{\partial z}+\frac{\omega_0^2 z^2}{4A_{11}}$$

$$\tilde{H}^{(2)}_{2,Z,b_{1,2}}=\frac{(-2A_{11}+2A_{12}\beta_{12}^{(0)})(a_{1,2}^{(0)})^2\hbar^2}{2d^2}\frac{\partial^2}{\partial b_{1,2}^2}+\frac{(-A_{11}-A_{12}\beta_{12}^{(0)})\hbar^2}{4}\frac{\partial^2}{\partial Z^2}-\frac{A_{12}2\hbar^2(a_{12}^{(0)})^2}{2d}\frac{\partial^2}{\partial b_{1,2}\partial Z}$$

$$+\frac{\omega_0^2 Z^2}{A_{11}}+U_{frv}^{(2)} \quad (88)$$

$$U_{frv}^{(2)}=\frac{M_1\omega_{0,12}^2}{4}[\frac{db_{1,2}}{\rho_1}]^2 \quad (89)$$

$\tilde{H}_{2,z,m}$ (one displaced harmonic oscillator) decouples from $\tilde{H}^{(2)}_{2,Z,b_{1,2}}$ (two coupled harmonic oscillators). Then, $f_{E,m} = f_1(z)f_2(Z, b_{1,2})$ implements the decoupling. The resulting decoupled Schrodinger equations can be solved by standard methods [7]. $\tilde{H}_{2,z,m}f_1 = E_1 f_1$ gives rise directly to the frequency: $\omega_z = \omega_0[1-(A_{12}/A_{11})\beta_{12}^{(0)}]^{1/2}$. $\tilde{H}^{(2)}_{2,Z,b_{1,2}}f_2 = E_2 f_2$ yields directly a quadratic equation for the squared frequencies $\omega^2_{Z,b_{1,2}}$, which has two solutions: $\omega^2_{Z,b_{1,2,+}}$ and $\omega^2_{Z,b_{1,2,-}}$. From the two explicit expressions for $\omega^2_{Z,b_{1,2,+}}$ and $\omega^2_{Z,b_{1,2,-}}$, one eliminates $\omega^2_{0,12}$. Then, by using the last equation and the above one, providing ω_z, one eliminates ω_0. That yields Eqs. (29) (30), in which all quantities are measurable and known experimentally. Notice that all vibrational frequencies, being independent on m, are given solely by $\tilde{H}^{(2)}_{2,frv,1}$.

The counterpart of Eq. (29) with ρ_2 replaced by the contribution coming from the model with potential $V^{(1)}_{j,j+1} = 2^{-1}B_{j,j+1}\omega^2_{0,j,j+1}(|\mathbf{y}_j+\mathbf{y}_{j+1}|-d_{j,j+1})^2$ (considered in Appendix G) has also been obtained. It will be omitted, because its comparison with experimental values appears somewhat less favourable than that for the potential $V^{(2)}_{j,j+1}$.

G *Comparison with other models for freely-rotating chains: 3D*

Let the potentials between units which are next-to-nearest neighbours be: $V^{(1)}_{j,j+1} = 2^{-1}B_{j,j+1}\omega^2_{0,j,j+1}(|\mathbf{y}_j+\mathbf{y}_{j+1}|-d_{j,j+1})^2$ (instead of $V^{(2)}_{j,j+1}$ in Subsections 3.2 and 4.2). $\omega_{0,j,j+1}$ are other frequencies, $d_{j,j+1}$ are lengths such that $|d_j - d_{j+1}| \le d_{j,j+1} \le d_j + d_{j+1}$ and $B_{j,j+1}(M_j^{-1}+M_{j+2}^{-1}) = 1$. Based upon and Eqs. (1), (19) (with $V^{(2)}_{j,j+1}$ replaced by $V^{(1)}_{j,j+1}$) and (18), a previous variational computation [30] using Eq. (59), has led to a model for an open freely-rotating chain, in which all d_j and $d_{j,j+1}$ be given constants. The variational wavefunction Φ_{σ_1} in [30] is chosen as:

$$\Phi_{\sigma_1} = \phi_{nn}(y)\phi_{nnn}(\mathbf{y})\psi_\sigma(\theta,\ \varphi)\,, \tag{90}$$

$$\phi_{nnn}(\mathbf{y}) = \prod_{l=1}^{N-2} \phi_{l,l+1},\ \phi_{l,l+1} = [\frac{\omega_{0,l,l+1}B_{l,l+1}}{\pi\hbar}]^{1/4} \exp[-\frac{\omega_{0,l,l+1}B_{l,l+1}}{2\hbar}(|\,\mathbf{y}_l + \mathbf{y}_{l+1}\,| - d_{l,l+1})^2]\,, \tag{91}$$

As all frequencies $\omega_{0,l}$ and $\omega_{0,l,l+1}$ become suitably large, localized Gaussians approach Dirac delta functions: $|\phi_{nn}(y)|^2 \to w_{rad} = [\prod_{l=1}^{N-1} d_l^{-2}\delta(y_l - d_l)]$ and:

$$|\,\phi_{nnn}(\mathbf{y})\,|^2 \to w_{ang} = [\prod_{l=1}^{N-2} \delta(|\,d_l\mathbf{u}_{y_l} + d_{l+1}\mathbf{u}_{y_{l+1}}\,| - d_{l,l+1})]\,. \tag{92}$$

The wavefunctions $\psi_\sigma(\theta,\ \varphi)$ (σ denoting quantum numbers) are arbitrary, except for: i) they are periodic in each φ_i with period $2\boldsymbol{\pi}$ and independent of any y_l, and ii) they are normalized with respect to the scalar product:

$$(\psi_1,\ \psi_2)_{3,fr} \equiv \int [\mathbf{d\Omega}]_3\, w_{ang}\psi_1(\theta,\ \varphi)^*\,\psi_2(\theta,\ \varphi), \tag{93}$$

One evaluates, as all frequencies $\omega_{0,i}$ $i = 1, \ldots, N-1$, and $\omega_{0,l,l+1}$ $l = 1, \ldots, N-2$, grow large, the quantum expectation value: $(\Phi,\ \tilde{H}\Phi)_3 \equiv \int \prod_{l=1}^{N-1} y_l^2 dy_l [\mathbf{d\Omega}]_3 \Phi(\mathbf{y})^* \tilde{H}\Phi(\mathbf{y})$ (recall Eq. (8)). This variational computation does not employ the approximations considered in Appendix D. The analysis in [30] was based, in turn, upon a previous quantum mechanical study for a closed-ring 3D freely-jointed molecular chain [28]. One finds, using Eq. (59) [30]:

$$(\Phi,\tilde{H}\Phi) = E_0 + (\psi_\sigma,\ (\tilde{H}_{3,fr} + O_{fr}(\hbar^2))\psi_\sigma)_{3,fr}\,, \tag{94}$$

$$(\psi_\sigma,\tilde{H}_{3,fr}\psi_\sigma)_{3,fr} = \int [\mathbf{d\Omega}]_3 \psi_\sigma^*(\theta,\ \varphi) w_{ang}\tilde{H}_{3,fr}\psi_\sigma(\theta,\ \varphi) = \int [\mathbf{d\Omega}]_3 \sum_{i,j=1}^{N-1} \frac{A_{ij}}{2d_i d_j}(\mathbf{e}_{3,i}\psi_\sigma(\theta,\ \varphi))^* \cdot w_{ang}(\mathbf{e}_{3,j}\psi_\sigma(\theta,\ \varphi) \tag{95}$$

for any normalized $\psi_\sigma(\theta,\ \varphi)$ fulfilling the above requirements. $\mathbf{e}_{3,l}$ is given in Eq. (7). $\mathcal{O}_{ang}(\hbar^2)$ (proportional to $\hbar^2$) denotes the set of all remaining contributions which do not depend on $\omega_{0,i}$ and $\omega_{0,i,i+1}$ and it does not contain angular differential operators acting upon $\psi_\sigma(\theta,\ \varphi)$: it will be disregarded here. Due to certain remarkable exact cancellations, E_0 (independent on θ, φ) equals the sum of the zero-point energies associated to all V_i and $V_{j,\,j+1}^{(1)}$ $E_0 = \sum_{i=1}^{N-1} 2^{-1}\hbar\omega_{0,i}$ + $\sum_{i=1}^{N-2} 2^{-1}\hbar\omega_{0,i,i+1}$. Such a E_0 appears to be at least a curious simplifying feature of the above choice $V_{j,\,j+1}^{(1)}$. The variational computation for $V_{j,\,j+1}^{(1)}$ summarized above [30] can be extended to $V_{j,\,j+1}^{(2)}$ from Subsection 4.2 (with the corresponding replacement of $|\mathbf{y}_l + \mathbf{y}_{l+1}| - d_{l,l+1}$ by $\beta_{l,l+1} - \beta_{l,l+1}^{(0)}$ in $\phi_{l,l+1}$). Then, one also arrives at Eq. (94), with another E_0 (depending on frequencies and on $\beta_{l,l+1}^{(0)}$) and $\mathcal{O}_{ang}(\hbar^2)$ but, crucially, with the same $\tilde{H}_{3,\,fr}$, which is satisfactory.

Anyway, another key property is that the frequency-dependent part of the new $(\Phi,\ \tilde{H}\Phi)$ (with $V_{j,j+1}^{(1)}$) is independent on both angles and angular differential operators. Whether such a frequency-dependent part for the new $(\Phi,\tilde{H}\Phi)$ (with $V_{j,\,j+1}^{(1)}$) depends on the constant $\beta_{i,i+1}^{(0)}$ could be not so important, as long as the former is just a variational bound. Physically, $|\mathbf{y}_j + \mathbf{y}_{j+1}| = [y_j^2 + y_{j+1}^2 + 2y_j y_{j+1}\beta_{j,j+1}]^{1/2}$ implies, after small vibrations approximations, that small oscillations of $|\mathbf{y}_j + \mathbf{y}_{j+1}|$ about $d_{j,\,j+1}$ are due to $b_{j,\,j+1}$ only for $V_{j,\,j+1}^{(2)}$, while to x_j, x_{j+1} and $b_{j,\,j+1}$ altogether for $V_{j,\,j+1}^{(1)}$. $\tilde{H}_{3,\,fr}$ and $\mathbf{e}_{3,l}$ are Hermitian operators (with respect to the scalar product in Eq. (93)) [30]. Using commutation rules (following partly from Eq. (59)), the total orbital angular momentum $\mathbf{L}_3 = \sum_{i=1}^{N-1}\mathbf{l}_i$ can be shown to commute with $\tilde{H}_{3,fr}$: see Appendix B in [30]. Recall that one Hamiltonian for the purely rotational motion of the fr chain was considered briefly in Subsections 4.2 and 4.3: recall Eq. (47). On the other hand, the above $\tilde{H}_{3,fr}$ could also be regarded in principle as an effective $3D$ quantum Hamiltonian for the unconstrained angular degrees of freedom of the freely-rotating chain, but the Dirac delta functions contained in ω_{ang} indicate that further analysis should be undertaken: see Appendix H.

H *D* = 3 *freely-rotating chains: effective Hamiltonian from Eq. (95) for N = 3*

The Hamiltonian in Eq. (95), due to the Dirac delta functions contained in ω_{ang}, poses an interesting problem. It will be analyzed here for $N = 3$, for simplicity. It will be convenient to change variables $(\theta, \varphi) \rightarrow (\theta, \varphi_0, \beta_{1,2})$. Then (with $\beta_{1,2} = \beta_{1,2}^{(0)}$):

$$\mathbf{e}_{3,i} = \mathbf{e}_{3,frv,r,i} + \mathbf{e}_{3,frv,v,i} \tag{96}$$

$\mathbf{e}_{3,frv,r,i}$ and $\mathbf{e}_{3,frv,v,i}$ are given in Eqs. (42) and (43), here with $b_{1,2}$ replaced by $\beta_{1,2}$ (which is harmless). For $N = 3$: $\mathbf{e}_{3,frv,v,i} = -i\hbar(\mathbf{u}_{l\neq i} - \beta_{1,2}^{(0)}\mathbf{u}_i)\frac{\partial}{\partial \beta_{1,2}}$. Then, making use here of the corresponding changes of variables in Subsection 4.2, Eq. (95) becomes, for $\psi_1 = \psi_2 = \psi$:

$$(\psi, \tilde{H}_{3,fr}\psi)_{3,fr} = (\psi,\ \psi)_{3,fr}^{-1}\int_0^{2\pi} d\varphi_0 \int d\beta_{1,2} \prod_{l=1}^{2}\int_0^{\pi} d\theta_l J_{3,fr} \sum_{i,j=1}^{2} \frac{A_{ij}}{2d_i d_j}$$

$$\times\, ((\mathbf{e}_{3,frv,r,i} + \mathbf{e}_{3,frv,v,i})\psi)^* \cdot \delta(\beta_{1,2} - \beta_{1,2}^{(0)})(\mathbf{e}_{3,frv,r,j} + \mathbf{e}_{3,frv,v,j})\psi)$$

$$= (\psi,\psi)^{-1}\int_0^{2\pi} d\varphi_0 \prod_{l=1}^{2}\int_0^{\pi} d\theta_l J_{3,fr} \sum_{i,j=1}^{2} \frac{A_{ij}}{2d_i d_j}((\mathbf{e}_{3,frv,r,i} + \mathbf{e}_{3,frv,v,i})\psi)^* \cdot (\mathbf{e}_{3,frv,r,j} + \mathbf{e}_{3,frv,v,j})\psi) \tag{97}$$

$\beta_{1,2}$ can be safely replaced by $\beta_{1,2}^{(0)}$ in Eq. (97), due to $\delta(\beta_{1,2} - \beta_{1,2}^{(0)})$. $J_{3,fr}$ is given in Eq. (65). $(\psi, \psi)^{-1}$ appears in Eq. (97) because ψ is now taken as unnormalized, for convenience while it was normalized in Appendix G. $(\psi, \tilde{H}_{3,fr}\psi)_{3,fr}$ in Eq. (97) is an integral over φ_0 and θ_l, $l = 1, 2$, containing $\psi(\varphi_0, \theta, \beta_{1,2}^{(0)}) \equiv \psi\,|_{\beta_{1,2}^{(0)}}$ and $(\partial\psi(\varphi_0, \theta, \beta_{1,2})/\partial\beta_{1,2})\,|_{\beta_{1,2} = \beta_{1,2}^{(0)}} \equiv \partial\psi/\partial\beta_{1,2}|_{\beta_{1,2}^{(0)}}$. The latter function is independent on and cannot be obtained from $\psi(\varphi_0, \theta, \beta_{1,2}^{(0)})$ and so the problem of a proper understanding of $(\psi, \tilde{H}_{3,fr}\psi)_{3,fr}$ and of the associated Schrodinger equation arises. One direct possibility consists in assuming $\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}} = 0$: then, one gets $\tilde{H}_{3,fr,3}$ (Eq. (47)) as an effective Hamiltonian for $3D$ rotational motions of the fr chain. However, the question still arises whether there are other possible effective Hamiltonians for the purely rotational motions of the $D = 3$ fr chain. In order to analyze them further, the well known variational approach [4] will be invoked. Let the functional $E[\psi\,|_{\beta_{1,2}^{(0)}}; \partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}]$ equal the complete right-hand-side in Eq. (97), which indicates how the variational approach should be interpreted and applied in order to arrive at an (eventually different) effective Schrodinger equation in the actual $3D$ situation. The functional $E[\psi\,|_{\beta_{1,2}^{(0)}}; \partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}]$ should be stationary for any small variation $\delta\psi\,|_{\beta_{1,2}^{(0)}}$ about the eigenfunction $\psi\,|_{\beta_{1,2}^{(0)}}$ and any small variation $\delta\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}$ about the associated independent function $\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}$. A standard variational calculation, extending directly the one in [4], gives:

$$\tilde{H}_{3,fr,eff}\psi\,|_{\beta_{1,2}^{(0)}} \equiv \frac{1}{2J_{3,fr}}\sum_{i,j=1}^{2}\frac{A_{ij}}{d_i d_j}(\mathbf{e}_{3,frv,r,i}^{+}J_{3,fr}[(\mathbf{e}_{3,frv,r,j}\psi\,|_{\beta_{1,2}^{(0)}} - i\hbar(\mathbf{u}_{l\neq j}-\beta_{1,2}^{(0)}\mathbf{u}_j)(\partial\psi/\partial\beta_{1,2})\,|_{\beta_{1,2}^{(0)}}]) = E\psi\,|_{\beta_{1,2}^{(0)}} \tag{98}$$

$$\sum_{i,j=1}^{2}\frac{A_{ij}}{2d_i d_j}(\mathbf{u}_{l\neq i}-\beta_{1,2}^{(0)}\mathbf{u}_i)(\mathbf{e}_{3,frv,r,j}\psi\,|_{\beta_{1,2}^{(0)}} - i\hbar(\mathbf{u}_{l\neq j}-\beta_{1,2}^{(0)}\mathbf{u}_j)(\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}) = 0 \tag{99}$$

Eq. (99) is a consequence of the fact that (ψ, ψ) does not depend on $\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}$, upon performing the variational copmputation. By eliminating the variational-approach-based (in general, non-vanishing) $\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}$ in terms of $\psi\,|\beta_{\beta_{1,2}^{(0)}}$ by using Eq. (99), Eq. (98) becomes

$$\tilde{H}_{3,fr,eff} = \sum_{i,j=1}^{2}\frac{A_{ij}}{J_{3,fr}2d_i d_j}[\mathbf{e}_{3,frv,r,i}^{+}J_{3,fr}[\mathbf{e}_{3,frv,r,j} - \frac{i\hbar(\mathbf{u}_{l\neq j}-\beta_{1,2}^{(0)}\mathbf{u}_j)\sum_{m,n=1}^{2}\frac{A_{mn}}{2d_m d_n}(\mathbf{u}_{l\neq m}-\beta_{1,2}^{(0)}\mathbf{u}_m)\mathbf{e}_{3,frv,r,n}}{\sum_{r,s=1}^{2}\frac{A_{rs}}{2d_r d_s}(\mathbf{u}_{l\neq r}-\beta_{1,2}^{(0)}\mathbf{u}_r)(\mathbf{u}_{l\neq s}-\beta_{1,2}^{(0)}\mathbf{u}_s)}]] \tag{100}$$

which yields an alternative effective Schrodinger equation for internal rotations in the $3D$ fr chain, for eigenfunctions $\psi\,|_{\beta_{1,2}^{(0)}}$ with eigenvalues $E(\tilde{H}_{3,fr,eff}\psi\,|_{\beta_{1,2}^{(0)}} = E\psi\,|_{\beta_{1,2}^{(0)}})$. Upon recalling Eq. (47), one sees in it the structure $(1/2J_{3,fr})\sum_{i,j=1}^{2}A_{ij}\frac{\mathbf{e}_{3,frv,r,i}^{+}}{d_i}J_{3,fr}\frac{\mathbf{e}_{3,frv,r,j}}{d_j}$, which appears in the right-hand-side of Eq. (100). For $D = 2$, similar (and simpler) developments also yield alternative effective Hamiltonians. For $D = 2$ and $N = 3$, the alternative effective Hamiltonian has the common structure $\frac{(A_{11}A_{12}\beta_{12}^{(0)}))\hbar^2}{2d^2}[-\frac{1}{2}\frac{\partial^2}{\partial\varphi_0^2}]$ plus a constant, depending on the choice of $\partial\psi/\partial\beta_{1,2}\,|_{\beta_{1,2}^{(0)}}$. That structure coincides with that in Eq. (87) (which contains such constant).

I *3D: total orbital angular momentum*

$\mathbf{L}_3$ (given in Section 2) is recast, in terms of $\theta_1, \ldots, \theta_{N-1}, \varphi_0$ and $\beta_{j,j+1}$ as:

$$\mathbf{L}_3 = i\hbar[\sum_{i=1}^{N-1}\frac{\mathbf{u}_{\theta_i}}{\sin\theta_i}]\frac{1}{N-1}\frac{\partial}{\partial\varphi_0} - i\hbar[\sum_{i=1}^{N-1}\mathbf{u}_{\varphi_i}\frac{\partial}{\partial\theta_i}|] \tag{101}$$

$\frac{\partial}{\partial\theta_i}|$ means differentiation for fixed φ_0, all θ_j (except θ_i) and all $\beta_{j,j+1}$. Several crucial cancellations implied that $\mathbf{L}_3$ is independent on all $\partial/\partial\beta_{j,j+1}$. The cartesian components of $\mathbf{L}_3$ do fulfill the standard commutation relations. A comparison of commutation rules involving $\mathbf{L}_3$ in Appendix B in [49] with Eq. (101) implies that $\mathbf{e}_{3,frv,r,i}$ and, hence, $\mathbf{e}_{3,frv,i}$ behave as vectors under rotations (as so does $\mathbf{e}_{3,frv,v,i}$). The same holds for $\boldsymbol{\pi}_{3,frv,i}$, so that $\boldsymbol{\pi}_{3,frv,i}\cdot\boldsymbol{\pi}_{3,frv,i}$ is a scalar and, hence, rotational invariant. This and Eq. (44) imply that:

$$(\psi, \tilde{H}_{3,frv}\psi)_{3,frv} = \int\prod_{l=1}^{N-1}d_l^2 dx_l[\mathbf{d\Omega}]_{3,fr}J_{3,fr}[\frac{1}{2}\sum_{i,j=1}^{N-1}A_{ij}(\boldsymbol{\pi}_{3,frv,i}\psi)^{*}\boldsymbol{\pi}_{3,frv,j}\psi + \psi_1^{*}(U_{fjv}+U_{frv})\psi_2] \tag{102}$$

is rotational invariant under a rotation $\psi \to [\exp i\alpha \mathbf{L}_3.\mathbf{n}]\psi$ of angle α about the unit vector $\mathbf{n}$, as so is $[d\Omega]_{3,fr} J_{3,fr}$. The same holds for $\tilde{H}_{3,fr,3}$ (Eq. (47)).

J 3D single-unit polymerization by classical fj chain at equilibrium: outline of computations

$f_2 = f_2(\boldsymbol{\pi}_{3,c,1}) = \int [d\Omega]_{3,L}\, f_{eq,2}$ will be studied here, by extending [32], [29]. First, the Gaussian integrations over $\prod_{i=2}^{N-1} d\varphi_i d\pi_{\varphi,c,i}$ in $[d\Omega]_{3,L}$ are performed, by generazing directly the rotational invariant methods in [32]. The result is, with $[\mathbf{d\Omega}]_{3,2} \equiv \prod_{l=2}^{N-1} d\varphi_l d\theta_l \sin\theta_l$:

$$f_2 = \exp[\frac{A_{12}^2 (A_2^{-1})_{22} \pi_{3,c,1}^2}{2K_B T}][\int \frac{[\mathbf{d\Omega}]_{3,2}}{(det\Delta_2)^{1/2}}]^{-1} \int \frac{[\mathbf{d\Omega}]_{3,2}}{(det\Delta_2)^{1/2}}$$

$$\times \exp[-\frac{A_{12}}{2K_B T} \sum_{i,j=2}^{N-1} (A_{12}(A_2^{-1})_{2i})(\pi_{3,c,1}\mathbf{u}_i)((\Delta_{2,1})^{-1})_{ij}(A_{12}(A_2^{-1})_{j2}(\pi_{3,c,1}\mathbf{u}_j)] \tag{103}$$

The $(N-2) \times (N-2)$ matrix A_2 with non-vanishing elements A_{ij}, $i, j = 2, \ldots, N-1$ is symmetric, tridiagonal and has positive eigenvalues. A_2^{-1} and $detA_2$ are the inverse and the determinant of A_2. The $(N-2) \times (N-2)$ matrices Δ_2 and $\Delta_{2,1}$ have elements: $(\Delta_2)_{ij} = (A_2^{-1})_{ij}\, \mathbf{u}_i\mathbf{u}_j$ and $(\Delta_{2,1})_{ij} = A_{12}(A_2^{-1})_{ij}\mathbf{u}_i\mathbf{u}_j$, respectively. The integral in Eq. (103), with $(\Delta_{2,1})^{-1} = 0$ has been studied in [32] and [29]: it was found that the dominant contributions are equal to one another and come from all tiny domains with $(\mathbf{u}_i\mathbf{u}_j)^2$ close to $+1$. One finds:

$$f_2 \simeq \exp[\frac{A_{12}^2 (A_2^{-1})_{22} \boldsymbol{\pi}_{3,c,1}^2}{2K_B T}][\int_0^{2\pi} d\varphi_2 \int_0^{\pi} d\theta_2 \sin\theta_2]^{-1} \int_0^{2\pi} d\varphi_2 \int_0^{\pi} d\theta_2 \sin\theta_2 \exp[-\frac{A_{12}^2 (A_2^{-1})_{22} (\mathbf{u}_2 \boldsymbol{\pi}_{3,c,1})^2}{2K_B T}] \tag{104}$$

A_{12} and $(A_2^{-1})_{22}$ account, respectively, for the influences of unit 2 and of all units 2, …, $N-1$ on the dynamics of unit 1. f_2 is a dimensionless function of $\frac{A_{12}^2 (A_2^{-1})_{22} \boldsymbol{\pi}_{3,c,1}^2}{2K_B T}$. Eq. (49) yields directly probability flux conservation ($W = f_1 f_2$):

$$\frac{\partial}{\partial t} \int d^3\boldsymbol{\pi}_{3,c,1} W = -\nabla_{\mathbf{y}_1} \int d^3\boldsymbol{\pi}_{3,c,1} [A_{11}\boldsymbol{\pi}_{3,c,1} - (K_B T)(\nabla_{\boldsymbol{\pi}_{3,c,1}} \ln f_2)]W) \tag{105}$$

$$\frac{\partial}{\partial t} \int d^3\mathbf{y}_1 \int d^3\boldsymbol{\pi}_{3,c,1} W = 0 \tag{106}$$

At this stage, after some numerical analysis, one approximates: $-(K_B T)(\nabla_{\boldsymbol{\pi}_{3,c,1}} \ln f_2) \simeq A_{12}\sigma\boldsymbol{\pi}_{3,c,1}$, $\sigma = -A_{12}(A_2^{-1})_{22}\sigma_1$, with another constant σ_1 (eventually, not strongly dependent on temperature): for the purposes of this work, $0 < \sigma_1 < 1$ suffices. A more detailed numerical assesment of σ_1 would follow from the analysis of

$$\int_0^{2\pi} d\varphi_2 \int_0^{\pi} d\theta_2 \sin\theta_2 \exp[-\frac{A_{12}^2 (A_2^{-1})_{22} (\mathbf{u}_2 \boldsymbol{\pi}_{3,c,1})^2}{2K_B T}],$$

to be omitted here.

Eq. (49) refers to the non-standard quantum Hamiltonian $\tilde{H}_{n-s,1}$. The direct counterpart of Eq. (49) for the standard quantum Hamiltonian $\tilde{H}_{eff,1} = -(\hbar^2/2)(A_{11} + A_{12}\sigma)\nabla^2_{\mathbf{y}_1} + U_1(|\mathbf{y}_1|)$, namely Eq. (50), will now be considered in outline in order to account for irreversibility in polymerization (say, unit 1 moving freely initially in the fluid will become attached for long time to unit 2 in the fj chain at equilibrium). The analysis of the quantum-mechanical evolution of a system towards thermal equilibrium is a difficult, multifarious and important problem in Non-equilibrium Quantum Statistical Mechanics, which has attracted and will continue to attract research activity. See for instance [50-55], [41] and references therein. Here, the procedure in [41] to approach approximately thermal equilibrium for long t will be followed, which will now be summarized.

Let $W_{eq}(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1})$ be the equilibrium Wigner function ($\partial W_{eq}/\partial t = 0$) of Eq. (50) for the standard quantum Hamiltonian $\tilde{H}_{eff,1}$. Let $H_{[n]}(\boldsymbol{\pi}_{3,c,1})$ ($[n] = (n_1, n_2, n_3)$, n_1, n_2, n_3 being non-negative integers) be the family of orthogonal polynomials determined by the (in general non-Gaussian) weight function W_{eq} by integrating over $\boldsymbol{\pi}_{3,c,1}$, for given $\mathbf{y}_1$ ($H_{[n]}(\boldsymbol{\pi}_{3,c,1})$ depend parametrically on $\mathbf{y}_1$). By introducing the non-equilibrium moments $W_{[n]} = W_{[n]}(\mathbf{y}_1, t) = \int d^3\boldsymbol{\pi}_{3,c,1} H_{[n]}(\boldsymbol{\pi}_{3,c,1}) W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1}, t)$, an infinite linear recurrence is obtained from Eq. (50) for moments $W_{[n]}$. The infinite linear recurrence is formally solved in terms of generalized operator continued fractions. Let: $W_{[0]} = W_{[0]}(\mathbf{y}_1, t) = \int d^3\boldsymbol{\pi}_{3,c,1} W(\mathbf{y}_1, \boldsymbol{\pi}_{3,c,1}, t)$ be the lowest moment. The long t approximation is implemented upon discarding moments higher than $W_{[0]}$ and performing long t approximations in the continued fractions, in physical conditions ressembling the regime of time and spatial distances adequate for polymerization. This procedure generalizes an analogous one in Classical Statistical Mechanics for the Liouville equation (see [41]). Then, the application of the long-time approximations in [41] to Eq. (50) for $\tilde{H}_{eff,1}$ leads to the following irreversible Schmolukowski equation ($\mathbf{y}_1 = (y_{1,1}, y_{1,2}, y_{1,3})$):

$$\frac{\partial W_{[0]}}{\partial t} = q_{eq}(A_{11} + A_{12}\sigma) \sum_{\alpha=1}^{3} \frac{\partial}{\partial y_{1,\alpha}} D M_{[1_\alpha],[0]} W_{[0]} \tag{107}$$

$$M_{[1_\alpha],[0]} W_{[0]} = -q_{eq}(A_{11} + A_{12}\sigma) \frac{\partial}{\partial y_{1,\alpha}} (\epsilon_{[2],[0]} W_{[0]}) + \frac{1}{q_{eq}} \frac{\partial U_1}{\partial y_{1,\alpha}} W_{[0]} \tag{108}$$

$D = D(y_1)$ being a diffusion coefficient. The equilibrium distribution is: $W_{[0],eq} = \Sigma_j \exp(-E_j/(K_B T))(\phi_j(\mathbf{y}_1)^* \phi_j(\mathbf{y}_1)$. $\varphi_j(\mathbf{y}_1)$ and E_j are, for all possible values of the set of subindices j, the continuum and bound-state eigenfunctions and energies of $\tilde{H}_{eff,1}(\tilde{H}_{eff,1}\phi_j(\mathbf{y}_1) = E_j\phi_j(\mathbf{y}_1))$. $W_{[0],eq}$ is seen to depend on $\mathbf{y}_1^2$, $\boldsymbol{\pi}_{3,c,1}^2$ and $(\mathbf{y}_1\boldsymbol{\pi}_{3,c,1})^2$. The operator $M_{[1_\alpha],[0]}$ and $\epsilon_{[2],[0]}$ appear naturally in the derivation of the linear recurrence for moments referred to above [41]. One has:

$$\epsilon_{[2],[0]} = -\int d^3\boldsymbol{\pi}_{3,c,1} W_{[0],eq})(\boldsymbol{\pi}_{3,c,1})_\alpha^2 / (q_{eq}^2 \int d^3\boldsymbol{\pi}_{3,c,1} W_{[0],eq})(< 0)$$

which is seen to be independent on $\alpha = 1, 2, 3$. U_1 depends only on y_1 and the same can be shown to hold for $\epsilon_{[2],[0]}$. Consequently and consistently, $W_{[0],eq}$ also fulfills: $M_{[1_\alpha],[0]} W_{[0],eq} = 0$, a set of three partial differential equations. The latter are compatible with one another and explicitly solvable for $W_{[0],eq}$, yielding an alternative representation for it, consistent with the above one as a sum over all eigenfunctions. Here, it suffices to infer approximate values of $\epsilon_{[2],[0]}$ (< 0), by using $W_{[0],eq}$ as the above sum over eigenfunctions. See [41]. For large y_1, the equilibrium distribution determined by W is approximated by the classical Boltzmann distribution, proportional to $\exp[-(K_BT)^{-1}(2^{-1}(A_{11} + A_{12}\sigma)\boldsymbol{\pi}^2_{3,c,1} + U_1)]$, which yields: $\epsilon_{[2],[0]} \simeq -1/2$. For very small y_1 (where U_1 can be expected physically to be repulsive), the contribution of $\epsilon_{[2],[0]}$ plays very little role and is disregarded. For medium and small y_1, one takes only the contributions of the bound states. If there is only one physically relevant bound state (to be assumed for simplicity), one can approximate $\epsilon_{[2],[0]} \simeq -(\hbar/q_{eq})^2(\delta y_1)^{-2}$, where δy_1 is a length scale characterizing approximately the smallest scale of appreciable variation of U_1. In the cases of physical interest, $\hbar/q_{eq}$ is adequately smaller than δy_1, so that $|\epsilon_{[2],[0]}|$ is also adequately smaller than 1/2. For qualitative studies, it may well suffice to accept that $|\epsilon_{[2],[0]}|$ is < 0 and is continuous and bounded.

$D = D(y_1)$ has been analyzed in [41]. From the latter, the following approximations follow. Let δU_1 be the average variation of U_1 (within its range, where $U_1 \neq 0$) in a scale δy_1. Let $|U_{1,0}|$ be the magnitude of $|U_1|$, averaged over the region where $U_1 < 0$. Then, δU_1 can be estimated to be about one order of magnitude smaller than $|U_{1,0}|$. Then, for large y_1, $D(y_1) \simeq (2^{1/2}(A_{11} + A_{12}\sigma)q_{eq})^{-1}\delta y_1$, while for or medium and small y_1, $D(y_1) \simeq [(\delta U_1(A_{11} + A_{12}\sigma))^{-1}]^{1/2}\delta y_1$.

K *3D freely-rotating linear chains with torsion constraints and vibrations*

For an energy scale somewhat smaller than those considered thus far, forces not only between pairs of nearest neighbours and pairs of next-to-nearest-neighbour units, but also between pairs of units located at positions j-th and $(j + 4)$-th are supposed strong enough to constraint the corresponding scalar products $\beta_{j,\,j+2} = \mathbf{u}_j\mathbf{u}_{j+2} = \cos\theta_j \cos\theta_{j+2} + \sin\theta_j \sin\theta_{j+2} \cos(\varphi_{j+2} - \varphi_j))$ to approximately fixed values $\beta^{(0)}_{j,\,j+2}$. This amounts to constrain torsions as well leading to a freely-rotating chain with constrained torsions (τ), with allowance for small oscillations. A short analysis for the latter will be outlined here, by omitting some minor direct details. The corresponding potentials $V^{(2)}_{j,\,j+2}$, $i = 1, 2$, generalize directly those in Subsection 3.2 and 4.2. Thus: $V^{(2)}_{j,\,j+2} = 2^{-1}B_{j,\,j+2}\,\omega^2_{0,\,j,\,j+2}(d_j\,d_{j+2}/d_{j,\,j+2})^2(\beta_{j,\,j+2} - \beta^{(0)}_{j,\,j+2})^2$. $\omega_{0,\,j,\,j+2}$ are other frequencies ($B_{j,\,j+2}$ being positive constants). For suitably large $\omega_{0,j,j+2}$, $\sum_{j=1}^{N-2} V^{(2)}_{j,j+2}$ hinders the angles between $\mathbf{u}_j$ and $\mathbf{u}_{j+2}$, $j = 1, \ldots, N - 2$ and, so, further internal rotations in the chain (namely, those which remained unconstrained in a fr chain). Then, one approximates: $\beta_{j,\,j+2} \simeq \beta^{(0)}_{j,\,j+2} + b_{j,\,j+2}$, with small $b_{j,\,j+2}$. $V^{(2)}_{j,\,j+2} \rightarrow V^{(2)}_{fr\tau v,\,j,\,j+2} = 2^{-1}B_{j,\,j+2}\omega^2_{0,\,j,\,j+2}(d_j\,d_{j+2}/d_{j,\,j+2})b_{j,\,j+2})^2$. One defines: $U^{(2)}_{fr\tau v} = \sum_{j=1}^{N-3} V^{(2)}_{fr\tau v,j,j+2}$. x, b_{nn} and φ_0 will be the same as before and $b_{nnn} = (b_{1,3}, \ldots, b_{N-3,N-1})$. Variables are changed as: $(x, \theta, \varphi) \rightarrow (x, \theta_1, \theta_{N-1}, \varphi_0, b_{nn}, b_{nnn})$. Then $\prod_{l=1}^{N-1} d_l^2 dx_l[\mathbf{d\Omega}]_3 \rightarrow \prod_{l=1}^{N-1} d_l^2 dx_l$ $[\mathbf{d\Omega}]_{3,fr\tau}J_{3,fr\tau}$, $[\mathbf{d\Omega}]_{3,fr\tau} = d\theta_1 d\theta_{N-1} d\varphi_0 \prod_{l=1}^{N-2} db_{j,j+1} \prod_{l=1}^{N-3} db_{j,j+2}$, with a new Jacobian $J_{3,\,fr\tau}$.

The new $3D$ scalar product of two wavefunctions $\psi_j = \psi_j\,(x, \theta_1, \theta_{N-1}, \varphi_0, b_{nn}, b_{nnn})$, $j = 1, 2$: is:

$$(\psi_1, \psi_2)_{3,frv\tau} \equiv \int_{-\infty}^{+\infty} \prod_{l=1}^{N-1} d_l^2 dx_l \int_0^{2\pi} \int_{-\infty}^{+\infty} \int_0^{\pi} [\mathbf{d\Omega}]_{3,fr\tau} J_{3,fr\tau} \psi_1^* \psi_2, \tag{109}$$

The molecular chain with those small radial and angular vibrations is described, by wavefunctions: $\psi = \psi_j\,(x, \theta_1, \theta_{N-1}, \varphi_0, b_{nn}, b_{nnn})$ (independent on θ_j, $j = 2, \ldots, N - 2$). The actual $3D$ counterpart of Eq. (39) is:

$$\boldsymbol{\pi}_{3,frv\tau,i} = -i\hbar\frac{\partial}{\partial x_i}\mathbf{u}_i + \frac{\mathbf{e}_{3,frv\tau,i}}{d_i} \tag{110}$$

$$\mathbf{e}_{3,frv\tau,i} = \mathbf{e}_{3,frv\tau,r,i} + \mathbf{e}_{3,frv\tau,v,i} \tag{111}$$

$$\mathbf{e}_{3,fr\nu\tau,r,i} = i\hbar\mathbf{u}_i - i\hbar\mathbf{u}_{\theta_i}(\delta_{1,i} + \delta_{N-1,i})\frac{\partial}{\partial\theta_i}| - i\hbar\mathbf{u}_{\varphi_i}\frac{1}{N-1}\frac{\partial}{\partial\varphi_0} \tag{112}$$

$$\mathbf{e}_{3,fr\nu\tau,v,i} = -i\hbar[(\mathbf{u}_{i-1} - \beta^{(0)}_{i-1,i}\mathbf{u}_i)\frac{\partial}{\partial b_{i-1,i}} + (\mathbf{u}_{i+1} - \beta^{(0)}_{i,i+1}\mathbf{u}_i)\frac{\partial}{\partial b_{i,i+1}}$$

$$+(\mathbf{u}_{i-2} - \beta^{(0)}_{i-2,i}\mathbf{u}_i)\frac{\partial}{\partial b_{i-2,i}} + (\mathbf{u}_{i+2} - \beta^{(0)}_{i,i+2}\mathbf{u}_i)\frac{\partial}{\partial b_{i,i+2}}] \tag{113}$$

$\delta_{1,i}\,\delta_{N-1,i}$ are Kronecker delta symbols ($\delta_{1,1} = 1$, $\delta_{1,i} = 0$ for $i \neq 1$). $\delta_{1,i}\,\delta_{N-1,i}\frac{\partial}{\partial\theta_i}|$ means differentiation with respect to θ_i for fixed φ_0, any $b_{i,\,i+1}$, any $b_{i,\,i+2}$ and any θ_j, $j \neq i$ and with the peculiarity that all such differentials for $i \neq 1, N-1$ do not contribute: that is, only $\frac{\partial}{\partial\theta_1}|$ and $\frac{\partial}{\partial\theta_{N-1}}|$ contribute. The approximate 3*D* Hamiltonian describing small "radial" vibrations about constrained distances between neighbours, next-to-near neighbours and next-to-next-to-near neighbours atoms along the molecular chain is assumed to be:

$$\tilde{H}^{(2)}_{3,fr\nu\tau} = \frac{1}{2J_{3,fr\tau}}\sum_{i,j=1}^{N-1} A_{ij}\boldsymbol{\pi}^{+}_{3,fr\nu\tau,i}J_{3,fr\tau}\boldsymbol{\pi}_{3,fr\nu\tau,j} + U_{fjv} + U^{(2)}_{frv} + U^{(2)}_{fr\tau v} \tag{114}$$

$\boldsymbol{\pi}^{+}_{3,fr\nu\tau,i}$ is the operator adjoint of $\boldsymbol{\pi}_{3,fr\nu\tau,i}$, with respect to the scalar product (109). $\tilde{H}^{(2)}_{3,fr\nu\tau}$ is Hermitean under Eq. (109). Eq. (115) describes a 3*D* vibrating quantum "rigid body". The "rigid body" orientation in 3*D* is described by θ_1, θ_{N-1}, φ_0, while (x, b_{nn}, b_{nnn}) account for the small vibrations. The corresponding vibrational frequencies, by using standard methods [7], are the solutions of algebraic equations of higher order requiring, in general numerical techniques. Simpler approximate Hamiltonians describing small "radial" vibrations about constrained distances between neighbours, next-to-near neighbours and next-to-next-to-near neighbours atoms along the molecular chain, omitting the complicated angular dependences in Eq. (115), are given in [11] (for DNA).

L *Branched chains and decoupling of branches*

Only one case will be outlined, extensions to other branched chains being direct. Let a $D = 3$ freely-jointed (fj) chain with small vibrations be formed by 8 units with masses m_i, at positions $\mathbf{R}_i$, $i = 1\ldots8$, with the following configuration. Unit 1 is fj to 2, 3 and 4, while unit 5 is fj to 4, 6, 7 and 8. First, the center-of mass is factored out like in all previous cases. For $j < i$, $|\mathbf{R}_j - \mathbf{R}_i|$ is approximately fixed at d_{ij}, with a small displacement x_{ij}. By extending Eq. (32) directly, one introduces: $\boldsymbol{\pi}_{3,fjvbc,ij} = -i\hbar\frac{\partial}{\partial x_{ij}}\mathbf{u}_{ij} + \frac{\mathbf{e}_{3,ij}}{d_{ij}}$. By extending directly U_{fjv} in subsection 4.1 and Eq. (33), the approximate Hamiltonian for the branched chain (*bc*) is:

$$\tilde{H}_{3,fjvbc} = \frac{(\boldsymbol{\pi}_{3,fjvbc,12} + \boldsymbol{\pi}_{3,fjvbc,13} + \boldsymbol{\pi}_{3,fjvbc,14})^2}{2m_1} + \frac{(-\boldsymbol{\pi}_{3,fjvbc,14} + \boldsymbol{\pi}_{3,fjvbc,45})^2}{2m_4} + \sum_{j=2,3}\frac{(-\boldsymbol{\pi}_{3,fjvbc,1j})^2}{2m_j}$$

$$+\sum_{j=6,7,8}\frac{(-\boldsymbol{\pi}_{3,fjvbc,5j})^2}{2m_j} + \frac{(\boldsymbol{\pi}_{3,fjvbc,56} - \boldsymbol{\pi}_{3,fjvbc,45} + \boldsymbol{\pi}_{3,fjvbc,57} + \boldsymbol{\pi}_{3,fjvbc,58})^2}{2m_5} + U_{fjv} \tag{115}$$

By following Eq. (31), a scalar product can be introduced here. Then, $\boldsymbol{\pi}_{3,\, fjvbc,ij}$ and $\tilde{H}_{3,\, fjvbc}$ are Hermitean under it. Next, let the units 2 and 3 be in the ground state of $\tilde{H}_{3,\, fjv,23} = \Sigma_{i,\, j=2,3} \frac{A_{ij}}{2} \boldsymbol{\pi}_{3,\, fjvbc,i}\, \boldsymbol{\pi}_{3,\, fjv,\, j} + \Sigma_{j=2,3} V_{fjv,\, j}$ with energy larger than $K_B T$. Then, the dynamics of the remaining units (1, 4, 5, 6, 7, 8) (prior to additional information on their energies) can be approximately decoupled from that of units 2 and 3. In fact, one can undertake another variational computation (say, a la Peierls), with $\Phi_{\sigma_1} = \phi_{2,3} \psi_\sigma(x, \theta, \varphi)$. $\phi_{2,3}$ is a variational normalized ground state wavefunction for $\tilde{H}_{3,\, fjv,23}$. $\psi_\sigma(x, \theta, \varphi)$ is a normalized generic wavefunction for units (1, 4, 5, 6, 7, 8). Upon evaluating

$$(\phi_{2,3}, [\frac{(\boldsymbol{\pi}_{3,\, fjvbc,12} + \boldsymbol{\pi}_{3,\, fjvbc,13} + \boldsymbol{\pi}_{3,\, fjvbc,14})^2}{2m_1} + \sum_{j=2,3} \frac{(-\boldsymbol{\pi}_{3,\, fjvbc,1j})^2}{2m_j} + \sum_{j=2,3} V_{fjv,\, j}] \phi_{2,3}) \tag{116}$$

crossed terms due to $(\boldsymbol{\pi}_{3,\, fjvbc,12} + \boldsymbol{\pi}_{3,\, fjvbc,13})$ times $\boldsymbol{\pi}_{3,\, fjvbc,14}$ give a vanishing contribution, by symmetric integration. The remaining terms give a variational upper bound for the ground state energy of $\tilde{H}_{3,\, fjv,23}$, $E_{var,23}$. What remains is an effective Hamiltonian for the units (1, 4, 5, 6, 7, 8):

$$\tilde{H}_{3,\, fjvbc23} = \frac{\boldsymbol{\pi}^2_{3,\, fjvbc,14}}{2m_1} + \frac{(-\boldsymbol{\pi}_{3,\, fjvbc,14} + \boldsymbol{\pi}_{3,\, fjvbc,45})^2}{2m_4} + \sum_{j=6,7,8} \frac{(-\boldsymbol{\pi}_{3,\, fjvbc,5j})^2}{2m_j}$$

$$+ \frac{(\boldsymbol{\pi}_{3,\, fjvbc,56} - \boldsymbol{\pi}_{3,\, fjvbc,45} + \boldsymbol{\pi}_{3,\, fjvbc,57} + \boldsymbol{\pi}_{3,\, fjvbc,58})^2}{2m_5} + U_{fjv} - \sum_{j=2,3} V_{fjv,\, j} + E_{var,23} \tag{117}$$