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Coherent dynamics in a butane molecule

Maira D'Alessandro,[1] Alexander Tenenbaum,[2,*] and Andrea Amadei[1]
[1]*Department of Chemical S&T, Tor Vergata University, Via della Ricerca Scientifica 1, 00133 Rome, Italy*
[2]*INFM Roma 1 and Physics Department, La Sapienza University, Piazzale Aldo Moro 2, 00185 Rome, Italy*
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We have simulated by molecular dynamics a single molecule of butane in a thermal bath at different temperatures. We have found that the collective degrees of freedom of the essential dynamics are endowed with quite different degrees of coherence, and that those subject to the largest fluctuations are also the most coherent, that is, the least chaotic. We suggest that this pattern may be characteristic also of larger molecules. A detailed assessment of the degree of coherence has been obtained by computing in the tangent space the whole set of generalized coherence angles.

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In recent years there has been a growing interest in the dynamics of biological macromolecules, and in the relation between collective motions in a macromolecule and its biological function. Myoglobin has been the subjet of particular interest, since experiment [1] and computer simulation [2,3] pinpointed a dynamical transition around 220 K. This transition separates a low-temperature region, where a harmonic description is appropriate, from a high-temperature region, where the molecule shows a combination of vibration within substates with transitions between them. In a very recent paper [4] the dynamics of myoglobin has been studied at very low temperature by molecular-dynamics simulation; the authors found a regime of selective energy exchange among normal modes. Their pattern is very similar to that found in a chain of nonlinear oscillators in the famous computer experiment performed by Fermi, Pasta, and Ulam [5], and its existence in a macromolecule was foreseen in a paper [6] published just at the same time as [4].

The dynamical regime found in myoglobin hints at the existence of ordered collective motions, at least at low temperature. Thus the question arises whether ordered collective motions exist also at room temperature, and whether they are relevant for the biological function of myoglobin (and possibly of a class of proteins). The best way to answer these questions would be a principal components analysis of the dynamics, which has shown the ability to extract from the total fluctuation of a macromolecule those components that are relevant to its biological function [7,8]. At low temperature the collective modes defined in this *essential dynamics* are very similar to normal modes; therefore, an ordered pattern similar to that found in [4] can be expected also in a principal component analysis performed at the same temperature. But the results at room temperature could be quite different, as the thermal vibrations could destroy the selective exchange of energy among modes. On the other hand, even a regular behavior of the first few principal components would not be a sufficient proof of an ordered collective behavior. Indeed, such a regular behavior has been shown to exist in high-dimensional random diffusion [9]. In that paper it is argued that an apparent cosinelike time evolution of the first few principal components of a protein may be an artifact due to a too short time scale of the simulation.

In order to gain some insight into the dynamical behavior of the principal components in a wide temperature range, we study a butane molecule in a thermal bath. Such a molecule can hardly be labeled as a macromolecule; nevertheless, it entails all the relevant degrees of freedom (DOFs) (stretching, bending, and dihedral torsion) that are found—in a much larger number—in a macromolecule. Because of its smallness, the convergence of the dynamics can be easily achieved within an affordable simulation time, and a detailed assessment of the chaotic character of each collective DOF can be performed.

A dynamic system with many DOFs that exhibits a chaotic behavior as a whole, may entail DOFs endowed with quite different levels of chaos. We have detected in previous works [10,6] such complex behavior in the dynamics of two-dimensional (2D) and three-dimensional (3D) Lennard-Jones microcrystals by performing molecular-dynamics computer experiments, and using the coherence angles (CAs) to measure the degree of chaos or order of each DOF. The CAs are the average angles between the directions corresponding to each DOF in the tangent space of the phase space of the system, and the direction characterized by the maximum Lyapunov exponent, i.e., the direction with the highest rate of divergence of near trajectories [10,6]. In the case of the 2D and 3D lattices the CAs were computed for a set of collective variables (normal modes); their spectrum revealed that at low temperature significant differences in coherence exist among the normal modes; these differences tended to disappear when the temperature of the system was raised and the total chaos increased. In the present work we show that different levels of chaos coexist even in the dynamics of a single simple molecule such as butane in contact with a thermal bath. The collective variables appropriate to exhibit the coexistence behavior in a butane molecule are the principal components used in the essential dynamics; these extended variables are derived by using the covariance matrix in a linear transformation of the Cartesian coordinates of the atoms [7].

We have used a united atoms model to represent the butane molecule (C_4H_{10}): the hydrogen atoms are incorporated

*Author to whom correspondence should be addressed. Electronic address: tenenbaum@roma1.infn.it

in the carbon atoms, giving four equally dressed point masses m [11,12]. As the mass of the molecule equals 58 a.m.u., each mass point is endowed with a mass of 14.5 a.m.u. $=24.08\times10^{-24}$ g. In our model the potential energy is the sum of three terms: the vibrational energy of the covalent bonds (stretching), the vibrational energy of the valence angles (bending), and the energy associated with the dihedral torsion. The stretching energy is represented [13] by a harmonic term: $V_s=\frac{1}{2}\Sigma_i k_1(b_i-b_0)^2$; [$b_0$ and b_i are, respectively, the equilibrium distance and the actual distance between atoms i and $i+1$ $(i=1,3)$]. The bending energy is represented [12] by a sum of quadratic terms of the cosine of the bending angles θ: $V_b=\Sigma_i k_2(\cos\theta_i-\cos\theta_0)^2$; θ_0 and θ_i are, respectively, the equilibrium angle and the actual angle between atoms i, $i+1$, and $i+2$ $(i=1,2)$. The potential energy entailed in the dihedral angle γ is represented [11] as $V_d=\Sigma_{j=0}^{5}a_j\cos^j\gamma$. V_d has an absolute minimum at $\gamma=0$, $V_d=0$ (gauche conformation), and two relative minima symmetrically located at $\gamma=\pm2/3\pi$, $V_d=2.926$ KJ/mol. This energy is equivalent to a temperature of 352 K, and corresponds to the trans conformation. The torsion potential is maximum at $\gamma=\pm\pi/3$, where it reaches the value $V_d=12.331$ KJ/mol, equivalent to a temperature of 1485 K [14]. The total force acting on each mass point i has been computed by $\mathbf{f}_i=-\boldsymbol{\nabla}_i(V_s+V_b+V_d)$, and the time evolution of the system has been simulated by molecular dynamics.

The computation of the explicit form of the forces in Cartesian coordinates is quite cumbersome; we report here the final results. Let $\mathbf{r}_i=\{r_{i,\alpha},\alpha=x,y,z\}$ be the position of the ith atom, and $\mathbf{b}_i=\mathbf{r}_{i+1}-\mathbf{r}_i$ $(i=1,2,3)$. We define

$$A_{i\alpha}=k_1(b_i-b_0)\frac{r_{i+1,\alpha}-r_{i,\alpha}}{b_i}.$$

The forces acting on the four atoms derived from the stretching potential V_S then have components $F_{1\alpha}=A_{1\alpha}$; $F_{2\alpha}=-A_{1\alpha}+A_{2\alpha}$; $F_{3\alpha}=-A_{2\alpha}+A_{3\alpha}$; $F_{4\alpha}=-A_{3\alpha}$. For the forces deriving from the bending potential V_b we write

$$\cos\theta_i=-\frac{\mathbf{b}_i\cdot\mathbf{b}_{i+1}}{b_i b_{i+1}}$$

and define

$$B_{i\alpha}=\frac{\partial\cos\theta_i}{\partial r_{i\alpha}}=\frac{1}{b_i}\left[\frac{r_{i+2,\alpha}-r_{i+1,\alpha}}{b_{i+1}}-\cos\theta_i\frac{r_{i+1,\alpha}-r_{i,\alpha}}{b_i}\right],$$

$$Ci\alpha=\frac{\partial\cos\theta_i}{\partial r_{i+1,\alpha}}=\frac{1}{b_{i+1}}\left[\frac{r_{i+1,\alpha}-r_{i,\alpha}}{b_i}-\cos\theta_i\frac{r_{i+2,\alpha}-r_{i+1,\alpha}}{b_i+1}\right],$$

$$D_i=-\frac{\partial V_b}{\partial\cos\theta_i}=-k_2(\cos\theta_i-\cos\theta_0).$$

These forces then have components $F_{1\alpha}=D_1B_{1\alpha}$; $F_{2\alpha}=D_1(-B_{1\alpha}+C_{1\alpha})+D_2B_{2\alpha}$; $F_{3\alpha}=-D_1C_{1\alpha}+D_2(-B_{2j}+C_{2\alpha})$; $F_{4\alpha}=-D_2C_{2\alpha}$. In order to compute the torsional forces we define two unitary vectors: $\mathbf{M}=\mathbf{b}_1\times\mathbf{b}_2$, $\hat{\mathbf{M}}=\mathbf{M}/M$; $\mathbf{N}=\mathbf{b}_2\times\mathbf{b}_3$, $\hat{\mathbf{N}}=\mathbf{N}/N$; for the dihedral angle γ we have then $\cos\gamma=-\hat{\mathbf{M}}\cdot\hat{\mathbf{N}}$. We define also $\mathbf{u}=(\hat{\mathbf{M}}+\hat{\mathbf{N}}\cos\gamma)/N$; $\mathbf{v}=(\hat{\mathbf{N}}+\hat{\mathbf{M}}\cos\gamma)/M$.

The torsional forces on the four atoms are then $\mathbf{F}_1=-R(\mathbf{b}_2\times\mathbf{u})$; $\mathbf{F}_2=R[(\mathbf{b}_1+\mathbf{b}_2)\times\mathbf{u}-\mathbf{b}_3\times\mathbf{v}]$; $\mathbf{F}_3=R[-\mathbf{b}_1\times\mathbf{u}+(\mathbf{b}_2+\mathbf{b}_3)\times\mathbf{v}]$; $\mathbf{F}_4=-R(\mathbf{b}_2\times\mathbf{v})$; with

$$R=\frac{\partial V_d}{\partial\cos\gamma}=\sum_{j=1}^{5}j\,a_j\cos^{j-1}\gamma.$$

In order to simulate the thermal bath we have used an iso-Gaussian thermostat, in which the total kinetic temperature is kept at a given value at each time step [16]. This thermostat is more efficient than the Nose'-Hoover one in sampling the phase space of a small molecule like the one at hand [17]. The equations of motion of the molecule in contact with the thermostat are $\dot{\mathbf{r}}_i=\mathbf{p}_i/m$, $\dot{\mathbf{p}}_i=\mathbf{f}_i-\xi(\mathbf{r},\mathbf{p})$, where $\mathbf{r}=\{\mathbf{r}_i\}$, $\mathbf{p}=\{\mathbf{p}_i\}$, and ξ is a variable that evolves in such a way that the total kinetic energy $\tilde{K}$ has the required constant value K. The expression for ξ is $\xi(\mathbf{r},\mathbf{p})=\Sigma_i\mathbf{p}_i\cdot\mathbf{f}_i/\Sigma_i|\mathbf{p}_i|^2$.

If the system has initially zero total momentum and zero total angular momentum, these values remain constant during the time evolution. The equations of motion of the mass points have been integrated with a modified leapfrog algorithm. It starts with the computation of interim momenta of the point masses at time t,

$$\tilde{\mathbf{p}}(t)=\mathbf{p}\left(t-\frac{h}{2}\right)+\frac{\mathbf{f}(t)h}{2}.$$

The momenta at time $t+h/2$ can then be computed by $\mathbf{p}(t+h/2)=2\tilde{\mathbf{p}}(t)\lambda-\mathbf{p}(t-h/2)$, where $\lambda=(K/\tilde{K})^{1/2}$ and $2\tilde{K}m=\Sigma_i\tilde{\mathbf{p}}_i^2(t)$. We have used a time step $h=1.06$ fs, which is 1/20 of the period T_s of the fastest vibration in the system, the stretching: $T_s=2.12\times10^{-2}$ ps. The precision of the algorithm is of $O(h^3)$ in the positions and in the velocities, and in a simulation at constant energy it would allow an energy conservation within 0.01%; moreover, it has the advantage of being symplectic [15]. The duration of the runs lasted between 10 and 20 ns. An initial interval of 0.1 ns was discarded in the statistics to avoid the influence of the initial conditions. The initial total momentum was set equal to zero. The temperatures simulated ranged from 140 K to 1080 K; in this range the dihedral angle can undergo transitions between the gauche and trans conformations.

We analyzed the dynamics of the butane molecule through the set of collective variables defined by means of the linear transformation of the vector $\mathbf{r}$ into $\mathbf{q}=O^T(\mathbf{r}-\langle\mathbf{r}\rangle)$, where O is the matrix of the columns which are the eigenvectors of the covariance matrix $C=\langle(\mathbf{r}-\langle\mathbf{r}\rangle)(\mathbf{r}-\langle\mathbf{r}\rangle)^T\rangle$; $\langle\cdot\rangle$ is a time average. O^TCO is a diagonal matrix, the elements of which are the eigenvalues corresponding to those eigenvectors. The time evolution of vector $\mathbf{q}$ displays

the essential dynamics of the molecule: it has been shown in the simulation of proteins that the components of $\mathbf{q}$ along few eigenvectors, corresponding to the largest eigenvalues of C, account for most of the total fluctuation [7,8]. The same matrix O can be used to compute the velocities associated with $\mathbf{q}$, through the transformation of $\dot{\mathbf{r}}=\{\dot{\mathbf{r}}_i\}$ into $\dot{\mathbf{q}}=O^T\dot{\mathbf{r}}$.

We resume briefly the analytical tools used to measure the degree of chaos (or order) of the DOFs of the system; a more general and detailed description of the theoretical framework can be found in [10,6]. Let $\mathbf{x}(t)=\{\mathbf{q}(t),\boldsymbol{\pi}(t)\}$ be the representative point of the system in phase space $\mathbb{R}^{6N}$, where $\boldsymbol{\pi}\equiv m\dot{\mathbf{q}}$ and N is the number of mass points in the system. Let $\mathbf{x}_1(0)$ and $\mathbf{x}_2(0)$ be two nearby points in $\mathbb{R}^{6N}$; the vector $\mathbf{w}(0)=\mathbf{x}_1(0)-\mathbf{x}_2(0)$ is a vector of the tangent space $T\mathbb{R}^{6N}$ of $\mathbb{R}^{6N}$. If the time evolution of $\mathbf{x}$ is generated by the set of differential equations $\dot{\mathbf{x}}=\mathbf{f}(\mathbf{x})$, then $\dot{w}_l(t)=\Sigma_{j=1}^{6N}\partial f_l/\partial x_j w_j(t)$, and a set of $3N$ coherence angles α_l can be defined through

$$\cos^2\alpha_l=\lim_{t\to\infty}\frac{1}{t}\int_0^t\frac{|\mathbf{w}^{(l)}(t')|^2}{|\mathbf{w}(t')|^2}dt',$$

where $\mathbf{w}^{(l)}(t)$ is the projection of $\mathbf{w}(t)$ on the plane TS_l of $T\mathbb{R}^{6N}$ that is spanned by the variations of $q_l(t)$ and $\pi_l(t)$; hereinafter we call DOFs the planes TS_l. α_l is an effective angle between TS_l and the direction of $T\mathbb{R}^{6N}$ associated with the highest divergence rate of near trajectories, i.e., with the maximum Lyapunov exponent λ_1. In a similar way, one can define and compute generalized CAs, α_{kl}, that measure an effective angle between the direction of $T\mathbb{R}^{6N}$ associated with the kth Lyapunov exponent and the subspace TS_l [6]. High (low) CAs characterize DOFs that are less (more) chaotic than the system as a whole. The set of generalized CAs measure the effective angles between each TS_l and the directions of $T\mathbb{R}^{6N}$ that induce a more chaotic (high Lyapunov exponent) or a more ordered behavior (low Lyapunov exponent). In [6] it was conjectured that the spectrum of α_{kl} should vary smoothly with k: that is, that $\alpha_{kl}\simeq\alpha_l$ for low values of k, corresponding to the most chaotic directions. We will show in the present work that this is indeed the case.

In Fig. 1 we report the eigenvalues of matrix C at three temperatures; the last three eigenvalues are zero, as they correspond to the exact constraint that does not allow the center of mass of the molecule to move. At $T=140$ K the first four eigenvalues are higher than all following ones; even though the values from the third one on do not differ greatly, it can be stated that the projection of the motion on the first four eigenvectors of C entails the largest portion of the total displacement. At higher temperature ($T=720$ K and $T=1080$ K) the distinction between the first three essential DOFs and the following ones becomes quite evident. How does this pattern reflect itself in the amount of coherence of these DOFs? In Fig. 2 we report the CAs of all 12 DOFs, computed for the collective variables q_l and π_l. This figure shows that there is a clear correspondence between the first few essential DOFs and the most coherent ones. At $T=140$ K the first four DOFs are more ordered than the system as a whole. At $T=720$ K and $T=1080$ K this correspondence is even more evident, as the first three essential DOFs correspond to eigenvalues that are much higher than the following ones; at the same time, these DOFs are more coherent than the system, while the remaining ones are more chaotic. The last three DOFs, corresponding to the constraint of the center of mass, have CAs equal to 90°; their value is constant in time, which can be construed to be a perfectly coherent dynamics. In Fig. 3 we report the generalized CAs α_{kl} at $T=1080$ K; the data are reported for the six expanding directions in $T\mathbb{R}^{6N}$ associated with the six largest Lyapunov exponents. For each DOF, the coherence angles between the DOF and the directions corresponding to Lyapunov exponents smaller than λ_1 vary smoothly with a decreasing value of the Lyapunov exponent. The pattern at

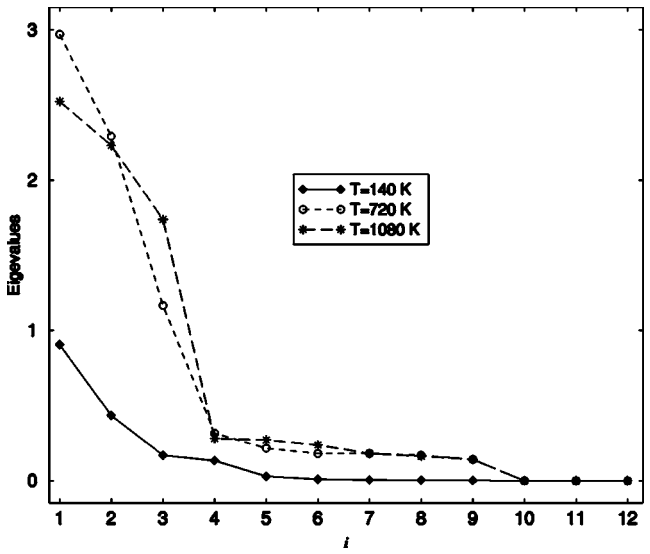

FIG. 1. Eigenvalues of the covariance matrix C in units of Å^2. i is the index of the eigenvalues that are ordered in decreasing magnitude.

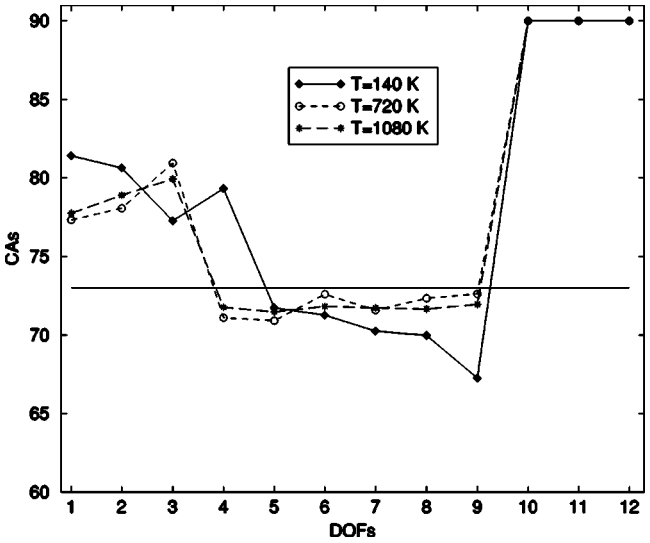

FIG. 2. Coherence angles α_l of the collective DOFs (q_l, $\dot{q}_l$); units are degrees. The straight line corresponds to the average angle $\alpha=73.2°$.

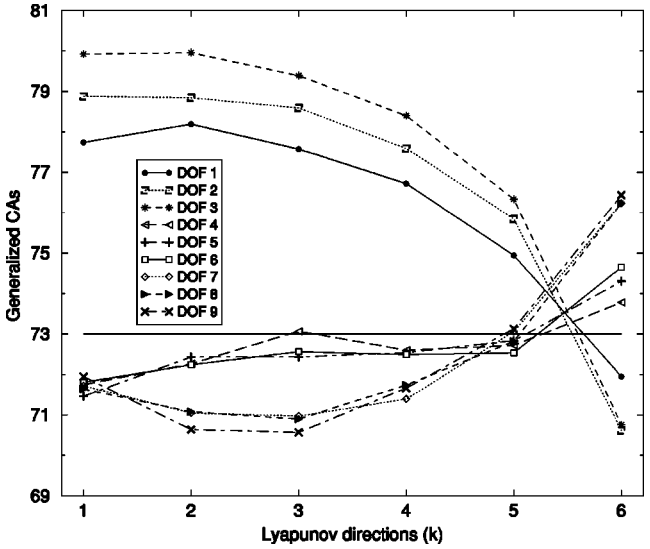

FIG. 3. Generalized coherence angles between the nonconstrained DOFs ($l=1,9$) and the six directions in the tangent space characterized by positive Lyapunov exponents λ_k. Units are degrees. The straight line corresponds to the average angle $\alpha=73.2°$. $T=1080$ K.

the two lower simulated temperatures (140 K and 720 K) is very similar: at 140 K (720 K) the curves corresponding to the first four (three) DOFs are above the average angle up to the fifth generalized CA, while the reverse is true for the curves corresponding to the following DOFs. This pattern was advanced as a conjecture in [6], and is confirmed here. The total coherence of a DOF depends on its angular distance in $T\mathbb{R}^{6N}$ from all characteristic Lyapunov directions (whether expanding or contracting), that is, on the generalized CAs. But in practice the level of chaos of a DOF is determined mainly by its orientation with respect to the most rapidly expanding directions. The results of Fig. 3 show that the average angle between a DOF and the most expanding direction (characterized by λ_1) is very similar to the average angle the same DOF makes with the directions that are just slightly less expanding, and very different in value from the average angle that the same DOF makes with the least expanding ones. Therefore, the single $\alpha_l \equiv \alpha_{1l}$ is already a convenient measure of the coherence of the lth DOF. The CAs, which are easily measured and interpreted in a computer experiment, summarize the information relevant to determine the coherence of the DOFs, as given in more detail by the generalized CAs.

We have shown that in a butane molecule the collective coordinates endowed with the largest fluctuations are also characterized by a higher coherence in their dynamics. Even though the butane molecule is small, it entails all internal DOFs—stretching of valence bonds, bending of valence angles, torsion of dihedral angles—that are found in much larger biomolecules. We speculate that in those large molecules one would find results similar to the pattern presented here, that is, that the principal components found in a covariance analysis are less chaotic than the molecule as a whole.

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