

# Characterization of liquid behaviour by means of local density fluctuations

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## Abstract

By means of principle component analysis of the local density fluctuations, as revealed by molecular dynamics simulations, we obtain detailed information on the relevant local density fluxes and corresponding spatial patterns.

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## 1. Introduction

In the past recent years, there has been a high interest in the structure and dynamical behavior of liquids. Pure water and water solutions have been widely studied either theoretically and experimentally because of their central role in chemistry, biology, industrial and natural sciences. Ohmine and Tanaka's [1] review focuses on theoretical characterization of collective motions, providing a detailed description of the strongly correlated molecular fluctuations in the hydrogen bond network in liquid water. Their work, as well as Ohmine and Saito's [2] extensively uses inherent structures (energy minima structures) analysis [3] in order to explain the collective motions in terms of some fundamental transitions. Moreover, the analysis of molecular auto and cross-correlation functions [4] provides information about the spatial extent of local oscillations and various relaxation mechanisms. However, at our knowledge, no studies based on the correlation of local molecular density fluctuations have been performed. In this work, we use the local density covariance (LDC) matrix, in order to characterize the local behavior of liquids. Principal component analysis has been extensively used in order to identify the most relevant internal motions of bio-macromolecules (Essential Dynam-

ics) [5–7]. In this work we use this approach to describe local density fluctuations in the study of molecular liquids, i.e. pure water and highly dilute water solutions.

## 2. Theory

If we decompose our system in  $n$  spherical concentric layers of identical volume and describe the instantaneous densities of the layers by means of the multidimensional vector  $\rho$ , we can write the LDC matrix as

$$\tilde{C} = \langle (\rho - \langle \rho \rangle)(\rho - \langle \rho \rangle)^T \rangle \quad (1)$$

where  $\langle \rangle$  denotes the (time) average. The symmetric matrix  $\tilde{C}$  can be diagonalised by an orthogonal transformation  $\tilde{O}$ :

$$\rho - \langle \rho \rangle = \tilde{O}q \quad (2)$$

$$q = \tilde{O}^T(\rho - \langle \rho \rangle) \quad (3)$$

which transforms  $\tilde{C}$  into a diagonal matrix  $\tilde{\Lambda}$  of eigenvalues  $\lambda_i$ :

$$\tilde{O}^T \tilde{C} \tilde{O} = \tilde{\Lambda} \quad (4)$$

$$\lambda_i = \langle q_i^2 \rangle \quad (5)$$

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Note that  $\tilde{O}$  is defined as

$$\tilde{O} = [\boldsymbol{\eta}_1, \boldsymbol{\eta}_2, \dots, \boldsymbol{\eta}_n] \quad (6)$$

where  $\boldsymbol{\eta}_i$  are the orthogonal eigenvectors of the covariance matrix  $\tilde{C}$ , given by the eigenvalues equation:

$$\tilde{C}\boldsymbol{\eta}_i = \lambda_i\boldsymbol{\eta}_i \quad (7)$$

It is possible to show that the covariance matrix eigenvectors are the directions, in multidimensional space, that maximize/minimize the density fluctuations. In fact, from the previous equations we have  $q_l = \boldsymbol{\eta}_l^T \Delta \boldsymbol{\rho} = \Delta \boldsymbol{\rho}^T \boldsymbol{\eta}_l$ ,  $\Delta \boldsymbol{\rho} = \sum_l \boldsymbol{\eta}_l q_l$ , and hence

$$\langle q_l q_j \rangle = \langle \boldsymbol{\eta}_l^T \Delta \boldsymbol{\rho} \Delta \boldsymbol{\rho}^T \boldsymbol{\eta}_j \rangle = \boldsymbol{\eta}_l^T \langle \Delta \boldsymbol{\rho} \Delta \boldsymbol{\rho}^T \rangle \boldsymbol{\eta}_j = \lambda_i \delta_{ij} \quad (8)$$

where  $\Delta \boldsymbol{\rho} = \boldsymbol{\rho} - \langle \boldsymbol{\rho} \rangle$ . If  $\sigma_v^2$  is the mean squared fluctuation of  $\boldsymbol{\rho}$  along an arbitrary unit vector  $\boldsymbol{\nu}$ , we can write

$$\begin{aligned} \sigma_v^2 &= \langle (\Delta \boldsymbol{\rho}^T \boldsymbol{\nu})^2 \rangle = \left\langle \sum_l \sum_r q_l \boldsymbol{\eta}_l^T \boldsymbol{\nu} q_r \boldsymbol{\eta}_r^T \boldsymbol{\nu} \right\rangle \\ &= \sum_l \sum_r (\boldsymbol{\eta}_l^T \boldsymbol{\nu}) (\boldsymbol{\eta}_r^T \boldsymbol{\nu}) \langle q_l q_r \rangle = \sum_l (\boldsymbol{\eta}_l^T \boldsymbol{\nu})^2 \lambda_l \end{aligned} \quad (9)$$

By sorting  $\lambda_i$  in decreasing order, we then have

$$\xi^2 \lambda_1 + \lambda_n (1 - \xi^2) \leq \sigma_v^2 \leq \xi^2 \lambda_1 + \lambda_2 (1 - \xi^2) \quad (10)$$

where  $0 < \xi^2 < 1$  is defined by  $\xi^2 = (\boldsymbol{\eta}_1^T \boldsymbol{\nu})^2$  and  $\lambda_n$  is the last eigenvalue. Rewriting the last disequality as

$$\xi^2 (\lambda_1 - \lambda_n) + \lambda_n \leq \sigma_v^2 \leq \xi^2 (\lambda_1 - \lambda_2) + \lambda_2 \quad (11)$$

we easily realize that  $\sigma_v^2$  has the maximum  $\sigma_v^2 = \lambda_1$  when  $\xi^2 = 1$ , as shown in Fig. 1. As a consequence, the unit vector that maximizes the mean squared fluctuation of  $\boldsymbol{\rho}$  is the first eigenvector  $\boldsymbol{\eta}_1$ . If we restrict our attention to the subspace orthogonal to  $\boldsymbol{\eta}_1$  and we perform the same procedure we obtain that  $\boldsymbol{\eta}_2$  is the direction that maximizes the mean squared fluctuation in that subspace. Thus, each eigenvector  $\boldsymbol{\eta}_i$ , is the direction that maximizes the mean squared fluctuation in the subspace  $\boldsymbol{\eta}_i, \boldsymbol{\eta}_{i+1}, \dots, \boldsymbol{\eta}_n$  but it is also the direction that minimizes it in the subspace  $\boldsymbol{\eta}_1, \boldsymbol{\eta}_2, \dots, \boldsymbol{\eta}_i$ .

### 3. Simulation methods

We have simulated pure water with a box of 256 SPC molecules [8] at 55.32 mol/l and 300 K. Moreover, we simulated three highly dilute solutions using the same water box but adding a chloride [9] ion, a sodium [9] ion and a methane [10] molecule, kept fixed in the centre of the box. All the simulations were performed using Gromacs software package [11] modified to use the isokinetic temperature coupling [12]. This was done in order to obtain results fully consistent with statistical mechanics [13,14]. The long-range electrostatics was calculated using the Particle Mesh Ewald (PME) [16] method, with 34 wave vectors in each

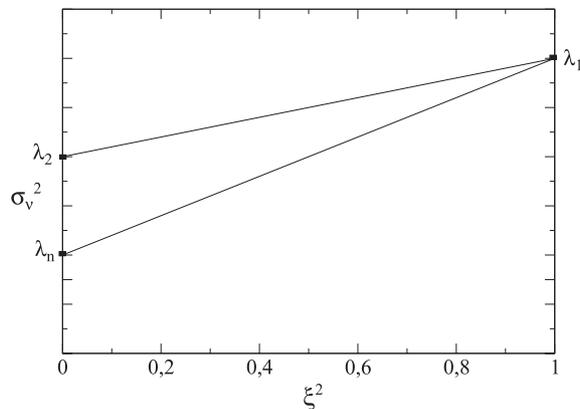


Fig. 1. Graph of the two straight lines that determine the extreme values of  $\sigma_v^2$ , as obtained using Eq. (11).

dimension and a fourth order cubic interpolation. Note that in the case of ionic solutions in the PME procedure the electrostatic interactions of the ion with its own replica is removed in order to achieve convergence. Such a condition corresponds to infinite dilution state. Short range interactions were evaluated within 0.9 nm cut-off radius. In each simulation (performed with a 2 fs time step) the initial 100,000 steps were used as equilibration run, and for the analysis a time length of 100 ns was employed.

### 4. Results

We have decomposed the simulation box in 100 spherical concentric layers of identical volume, starting from the center of the box. In the pure water (SPC) simulation, our reference condition, no constraints have been used and therefore water molecules were freely moving through the layers. For the other simulations, sodium, chloride and methane solutions, the solute was added constraining its position at the centre of the box, i.e. the centre of the spherical layers. In this paper our goal is the characterization of the local density patterns and fluctuations of liquid water for molecular fluxes relative to a spatial reference of frame as well as with respect to a fixed central molecule. Moreover, the use of different fixed central molecules (solutes) allows the direct comparison of their effects on the surrounding water fluxes.

In Fig. 2 the time averaged density in each layer is shown. From the figure it turns out that the local average density pattern is strongly affected by the type of fixed central molecule. The average density pattern of the pure water, where no fixed central molecule is present, is as expected completely constant. The values of the first maxima of the average density for the ionic solutions are higher than the one for methane, i.e. there are more solvent molecules near the ions because of the strong (electrostatic) solute-solvent interactions. The figure also shows that sodium ion, with smaller size, has denser solvation shells, in agreement with previous findings [15]. To investigate the

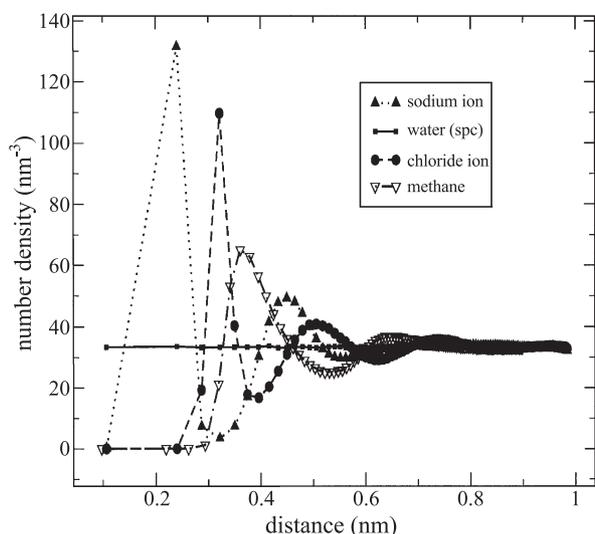


Fig. 2. Layer average molecular density ( $d$  is the distance from the geometric center of the simulation box).

density fluctuation behavior we use the LDC matrix. The eigenvalues obtained by diagonalisation of this matrix for the systems studied, are shown in Fig. 3. Most of the eigenvalues are rather similar implying that for all the systems there are many correlated density fluxes of similar amplitude and free energy variation. Only the first few eigenvalues (corresponding to the largest correlated spontaneous fluxes) and the last 10–15 eigenvalues (corresponding to almost constrained fluctuations) differ significantly from the other almost degenerate eigenvalues. Interestingly, the presence of the fixed central molecule seems to enhance such a difference for the first eigenvalues. As described in the theory section, in each eigenvector the components provide the density correlation of the layers.

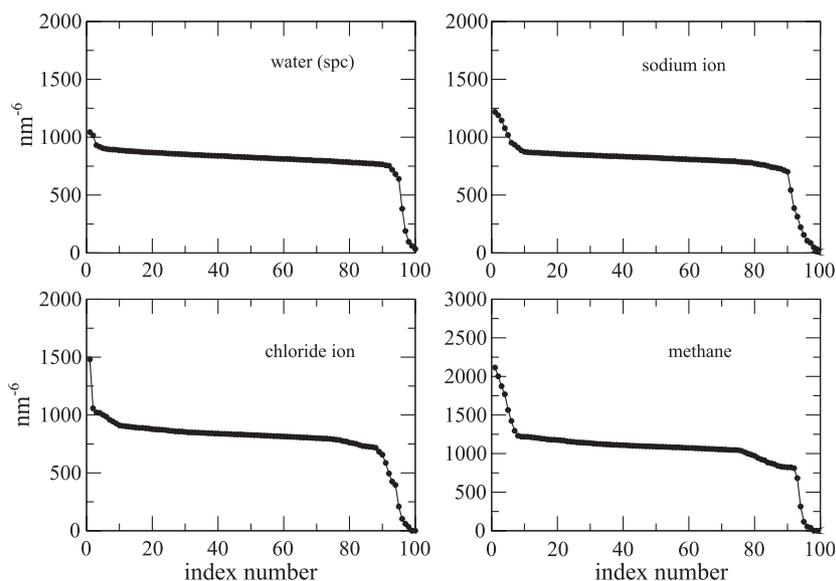


Fig. 3. Eigenvalues obtained from diagonalisation of LDC matrices.

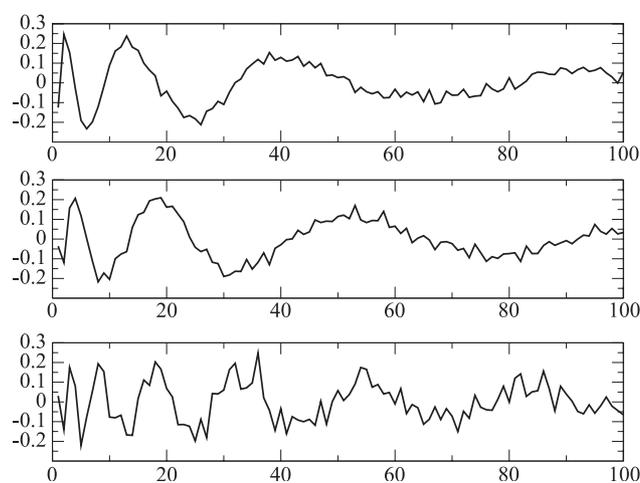


Fig. 4. Components of the first (first row), second (second row) and third (third row) eigenvectors of pure water versus the layer index.

In Fig. 4 we show the component patterns of the first three eigenvectors (providing the principal spontaneous density fluctuations) for the pure water simulation. The presence of a long-range correlation is evident, which extends all over the simulation box (2 nm), which is damped only in the last layers. Such fluxes involve anticorrelated density fluctuations for neighbouring subgroups of layers, each consisting of about five layers. Eigenvectors corresponding to smaller eigenvalues are defined by either anticorrelated fluctuations for each neighbouring layer (almost degenerate eigenvectors) or by a net fluctuation (i.e. without a relevant anticorrelation) only for a group of layers (almost constrained eigenvectors).

In Fig. 5 we show the different component patterns of the first three eigenvectors for the chloride, sodium and methane solutions as a function of the layer-index. From

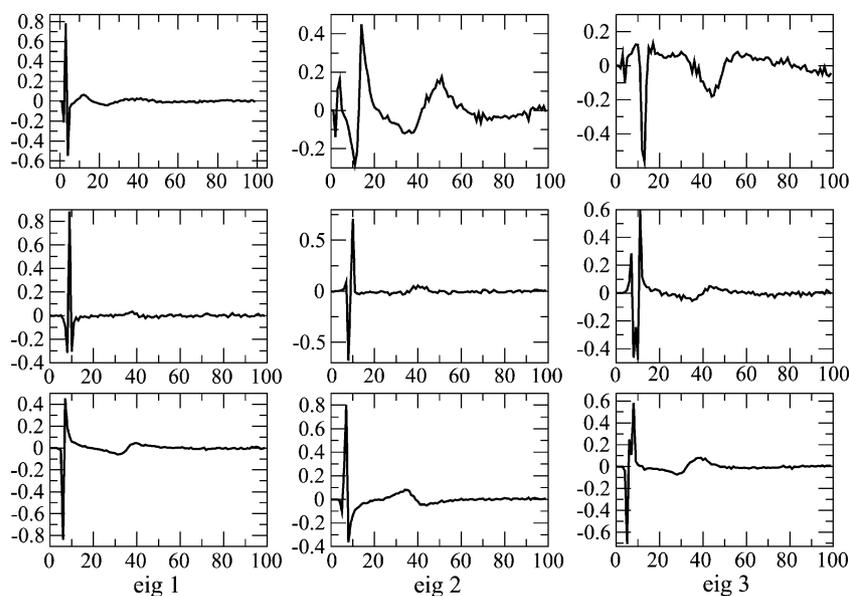


Fig. 5. Components of the first, second and third eigenvectors (from left to right) versus the layer index. First row: chloride ion solution. Second row: sodium ion solution. Third row: methane solution.

the comparison of this figure with the previous one it is clear that the solute (fixed central molecule) largely removes the long range correlations and the corresponding largest spontaneous fluctuations are mainly concentrated within the first hydration shells, i.e. the largest components correspond to layers 4–6 for chloride solution, to layers 7–10 for sodium solution and to layers 8–10 for methane

solution. It is worth noting that such a different behavior basically disappears when considering high-index eigenvectors. According to what was previously observed [15] the sodium ion induces a quite large rigid coordination shell of the surrounding water, as indeed shown in the figure by the fact that layers 1–6,  $d \approx 0\text{--}0.4$  nm, are nearly orthogonal to the first three eigenvectors. Interestingly, in the case of

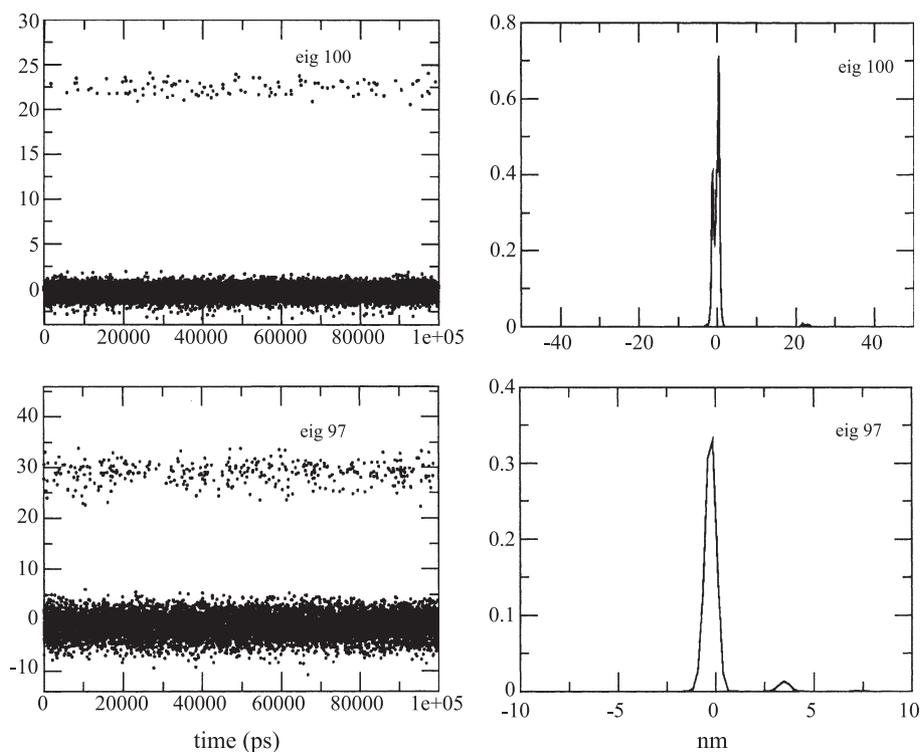


Fig. 6. Left side: Projection of the trajectory onto non Gaussian eigenvectors for sodium solution (up) and methane one (down) versus time. Right side: Probability distributions along the corresponding eigenvector for sodium solution (up) and methane one (down).

chloride and methane where the first hydration water molecules are less rigid, non-zero components of the first three eigenvectors are present even very close to the solute. It is also remarkable that except for minor differences, ions and methane seem to provide rather similar correlation patterns for density fluctuations. This shows that the main effect in the removal of the long range correlations is due simply to the presence of the fixed central molecule, regardless of its chemical nature.

Finally, in the pure water system the distribution of the fluctuations along all the eigenvectors are quite Gaussian (data not shown). This implies that fluctuations are statistically independent and the corresponding free energy surface is quadratic. For the other systems studied, where a fixed central molecule is present, we obtain essentially the same results except for the presence in the sodium and methane solutions of non-Gaussian fluctuations for eigenvectors 100 and 97, respectively (see Fig. 6). These high-index eigenvectors correspond to almost constrained density fluxes which simply change the solvent molecular density in the first solvation shell with a double state regime.

## 5. Conclusions

In this paper we investigated the local fluxes of liquid water as obtained by means of principal component analysis of density fluctuations. Our results show the presence of a characteristic long-range correlation pattern when no fixed central molecule is considered, i.e. density fluxes are defined with respect to a spatial reference of frame. Such spontaneous long-range fluctuations are largely suppressed when density fluxes are defined with respect to a fixed central molecule, which essentially constrains the main density fluctuations within the first hydration shells. Moreover, for all the systems studied a large part of the correlated flux modes (eigenvectors) are almost degenerate (i.e. very similar eigenvalues) and relevant differences are present

only within the first few eigenvectors. Finally the comparison of the systems where a fixed central molecule is used shows that different central molecules provide very similar behaviours of the surrounding water molecules, at least as far as density fluctuations are concerned. This clearly means that the main effect in the removal of the long-range correlations is due simply to the presence of the fixed central molecule, regardless of its chemical nature.

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