



Thermal stability of water up to super-critical states: Application of the singular value decomposition and grund functions



Philipp J. di Dio*

Institute of Mathematics, University of Leipzig, Augustusplatz 10, D-04109 Leipzig, Germany

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ABSTRACT

In the present work a systematic investigation of temperature on the dynamic structure of water and noble gases is given and a simple formula for the temperature dependent distribution functions with two terms is gained. The singular value decomposition tool is applied to temperature dependent radial and spatial distribution functions to decompose them into linear combinations of distant dependent grund radial/spatial distribution functions $g_i(r)$ and temperature dependent coefficients $c_i(T)$. The method condenses information from a large amount of data into a much smaller and manageable amount without loss of information. For the test systems (TIP3P water and noble gases with different force fields), the main temperature changes are condensed into the second grund function g_2 and its coefficient c_2 . c_2 obeys the Boltzmann distribution law and altogether we find that

$$g(r, T) \approx g_c(r) + e^{-\frac{r}{D}} \cdot g_t(r)$$

in a temperature range of more than 700 K. We introduce the new property of the thermal stability and the thermal stability energy D . This single energy and the grund functions characterize the structural changes (e.g., hydrogen bonds) in liquids from ambient temperatures up to supercritical states.

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1. Introduction

Every dynamic structure is temperature dependent, but only a small number of temperature effects in complex systems are accurately described. Especially for the liquid and gaseous structure and its temperature dependence there is a lack of mighty analysis tools to gain deeper insights into their structural behavior and the underlying processes governing their structure. Recently, it was shown that singular value decomposition (SVD) paves the way for a unified analysis of temperature dependent radial distribution functions (RDFs) [1] as a linear combination:

$$g(r, T) = c_1(T) \cdot g_1(r) + c_2(T) \cdot g_2(r) + \dots \quad (1)$$

The present paper unifies and extends the application of the SVD tool.

The SVD method is widely applied in many fields with different aims, e.g., calculation of the Moore–Penrose–pseudoinverse, noise filtering, and principle component analysis in analytical chemistry [2], astronomy [3], biochemistry [4], biology [5], organic chemistry [6], physical chemistry [7], physics [8], and theoretical chemistry [9], as well as the continual application in signal processing [10–13]. For a review about the early history of the singular value decomposition, see for example Ref. [14].

In the present study, TIP3P water and Lennard–Jones noble gases are used as test systems for the SVD tool in connection with temperature dependent RDFs and its decomposition into grund RDFs (GRDFs). An exorbitant number of experimental and theoretical studies about pure water, solvation, solutions, and mixtures are published. Temperature and pressure dependent structural changes are frequently of interest [15–30], but no systematic approaches (especially with SVD) to generalize the changes in liquids with temperature have been done before.

In 1992, Corongiu and Clementi published a study about temperature dependent water in a temperature range from 238 to 368 K [15]. Therein, molecular dynamics simulations of water with the “Nieser–Corongiu–Clementi flexible water molecules” were performed to study structural properties such as RDFs. The differences

$$\Delta g_{00}(r, \Delta T) := g_{00}(r, T_1) - g_{00}(r, T_2) \quad (2)$$

with $\Delta T := T_1 - T_2$ and

$$\frac{\Delta g_{00}(r, \Delta T)}{\Delta T} \quad (3)$$

were calculated and plotted. Especially from Eq. (3) it was found that the temperature changes in the RDFs from 238 to 368 K are proportional to ΔT , i.e., Eq. (3) depends linearly on ΔT for fixed r .

In 2005 and 2006, Mantz et al. published two studies about temperature dependent water with special emphasis on the temperature dependence of SDFs [16,17]. They used different classical

* Tel.: +49 3419732328.

E-mail address: didio@uni-leipzig.de.

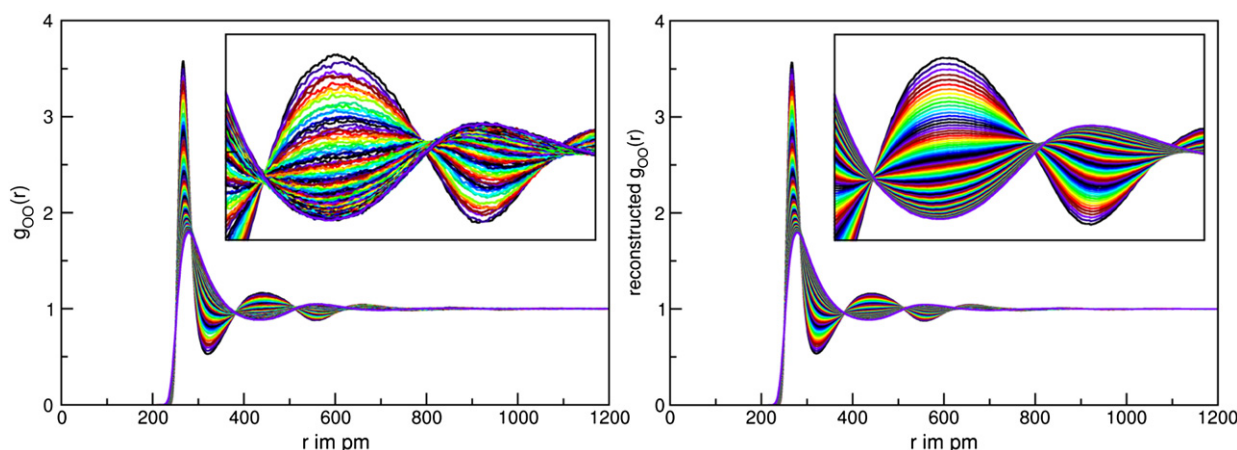


Fig. 1. Left: oxygen–oxygen radial distribution functions $g_{OO}(r)$ of TIP3P water between 275 and 1000 K every 5 K. Right: reconstructed oxygen–oxygen radial distribution functions $g_{OO}(r)$ of TIP3P water between 275 and 1000 K every 5 K from the first four GRDFs and the fitted coefficients. Temperature labels are omitted for clarity.

force fields (AIP1, TIP3P, TIP3P-ice, TIP4P, TIP4P-pol-2, and TIP5P) to calculate the water SDFs at 300 and 353 K. Unfortunately, the temperature dependence of the SDFs could only be compared at these two temperatures. A representation of the changes over the whole temperature range was not possible.

The SVD tool, which will be introduced in this work, will simplify and extend the analysis of these results as well as give further insights into the underlying laws governing the structure of liquids independent on the level of theory.

Many theories describing liquids exist. They describe the thermodynamic properties of liquids over a large temperature range sufficiently. Among these theories, statistical mechanics seems to be best suited for dynamical many body systems like molecular dynamics simulations. Unfortunately, statistical mechanics is very general and in applications serious approximations of the systems are needed to determine analytical expressions or numerical results. This renders a discussion of special effects in complicated liquids like water impossible. Recently, the analytic expression

$$g(r, T) = \frac{R_b^3 - d^3}{3r^2} \cdot \frac{P(r, T) \cdot e^{-\frac{u(r)}{k_B T}}}{\int_d^{R_b} P(r, T) \cdot e^{-\frac{u(r)}{k_B T}} dr} \quad (4)$$

with

$$P(r, T) = \sum_{l=1}^{\infty} e^{-\frac{(l-1/2)^2 \pi^2}{8r^2 \mu k_B T}} \cdot \sin^2 \left((l-1/2) \pi \frac{r-d}{r_f} \right) \quad (5)$$

has been derived by Zhao et al. [31,32] using the “identical particle in quasi-mean potential energy fields” assumption, i.e., only pair potentials are considered, and it is only valid for monoatomic, spherically

Table 1
First seven singular values s_i and reduced singular values \tilde{s}_i from all OO-, OH-, and HH-RDFs in the temperature range from 275 to 1000 K.

i	OO-RDFs		OH-RDFs		HH-RDFs		
	s_i	\tilde{s}_i	s_i	\tilde{s}_i	s_i	\tilde{s}_i	
1	341.579	13.0749	331.458	15.9964	331.324	27.7358	Main contributions
2	26.125	1.0000	20.721	1.0000	11.946	1.00080	
3	1.275	0.0488	1.571	0.0758	1.457	0.1219	Minor contributions
4	0.666	0.0255	0.199	0.0096	0.272	0.0228	
5	0.161	0.0062	0.087	0.0042	0.092	0.0077	Negligible perturbations and noise
6	0.136	0.0052	0.075	0.0036	0.057	0.0048	
7	0.115	0.0044	0.055	0.0027	0.045	0.0037	
⋮	⋮	⋮	⋮	⋮	⋮	⋮	

symmetric, and non-polar molecules. In Eqs. (4) and (5) $u(r)$ is the pair potential, d is the minimum molecular diameter, R_b is the boundary radius of free relative motion for dense fluids, r_f is the free moving radius of one molecule to the reference molecule, μ is the reduced mass, h is the Planck constant, and k_B is the Boltzmann constant. These equations will justify several results of the following SVD approach, e.g., give hints for an appropriate choice of fitting functions for the temperature dependent coefficients $c_i(T)$.

Another open problem is the temperature dependence of coarse-grained force fields, i.e., the absence of temperature transferability of the iterative Boltzmann inversion (IBI) [33]. The IBI constructs iteratively potentials $V_i(r)$ by

$$V_{i+1}(r) = V_i(r) + k_B T \ln \frac{g^i(r)}{g(r)} \quad (6)$$

which are simpler than the original force fields (or experiments) to save computer (or measurement) time. Unfortunately, in this procedure only one temperature and one calculated or experimental RDFs $g(r)$ at this fixed temperature are used. The resulting coarse-grained force field is often temperature dependent and does not reproduce the RDFs at different temperatures. One way to remove the lack of temperature transferability is to expand the IBI to temperature dependent RDFs. Hence, a simple and unique method is presented to decompose and interpolate temperature dependent RDFs in such a way that the IBI in Eq. (6) can be expanded to temperature dependent RDFs in a subsequent step.

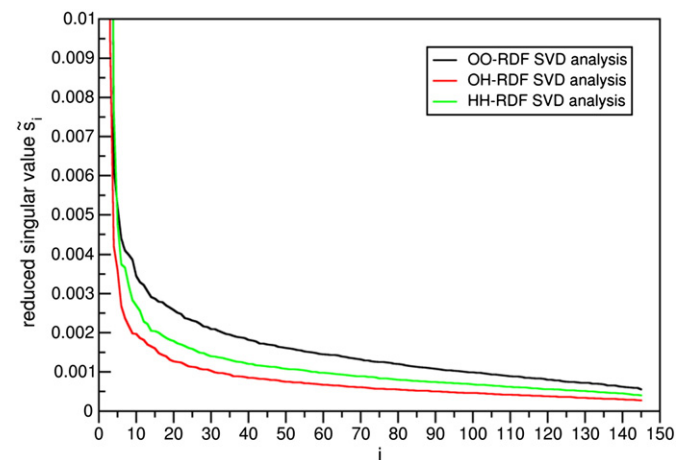


Fig. 2. Reduced singular values \tilde{s}_i for all TIP3P water RDF SVD analyses.

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