

ADDITIONS AND CORRECTIONS

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Ruchi Sharma, Charusita Chakravarty,* and Edoardo Milotti: Multiple Time Scale Behavior and Network Dynamics in Liquid Methanol

Page 9071. We have discovered an error in the computation of the tagged particle potential energies for the results presented in ref 1. The tagged potential energy (TPE), u_i , of the i th particle is defined as the interaction energy of particle i with all other particles in the system. The different contributions to the TPE, u_i , are given by²

$$u_i = u_i^{\text{vdW}} + u_i^{\text{rec}} + u_i^{\text{screen}} - u_i^{\text{self}} \quad (1)$$

where u_i^{vdW} , u_i^{rec} , u_i^{screen} , and u_i^{self} are the van der Waals, Ewald reciprocal space, Ewald real space, and Ewald self-correction terms, respectively. While computing the TPE, the number of neighbors were not correctly counted for u_i^{vdW} and u_i^{screen} . The contribution due to long-range interactions, u_i^{rec} , and the self-correction term, u_i^{self} , were correctly computed. The ensemble averages of the TPE, $\langle u \rangle$, and the total potential energy, U , were computed correctly. In our paper, we studied both the static tagged potential energy distribution, $P(u)$, and the associated power spectra, $S_u(f)$, defined in eq 1 of the original paper. Correcting the computational error does not lead to any qualitative changes in the power spectra, $S_u(f)$, but significantly modifies the static distributions, $P(u)$. In this erratum, we provide revised versions of the key figures; extensive details are provided elsewhere.³

Figure 1 of the original paper remains unchanged.¹ Figure 2 of the original paper is replaced by Figure 1 and shows the static distribution, $P(u)$, of the tagged molecule potential energies, $u(t)$, for methanol at several temperatures along the 0.768 and 0.878 g cm⁻³ isochores. Comparison with the earlier version of Figure 2 shows that the multimodality of the static TPE distributions disappears to give a unimodal distribution, though the mean value of tagged particle energies does not change. A second peak emerges as the temperatures are lowered along both of the isochores. The distributions are typically non-Gaussian with nonzero third and fourth moments. Since the changes in the $P(u)$ distributions will be the same for Figures 3 and 7a in the original paper, we do not reproduce the corrected version of these figures here, though they are available in ref 3.

The effect of the above error on the $S_u(f)$ power spectra of both methanol and water is small, as shown in Figure 2, which replaces Figure 4 of the original paper. The qualitative features remain the same, with high-frequency peaks due to librations, a multiple time scale (MTS) region at intermediate densities and a crossover to white noise at low frequencies. The location of the librational (restricted rotation) peak for H1 methanol and for SPC/E water remain the same. The MTS regime in methanol at 300 K and 0.768 g cm⁻³ which earlier was from 0.2 to 200 cm⁻¹ now shifts from 1 to 200 cm⁻¹; i.e., there is a slight shift in the crossover to white noise. The α value for the 0.2–40 cm⁻¹ range, which was 1.36 earlier, is now 1.22 for the 1–40 cm⁻¹ range, while for 40–200 cm⁻¹ it is 1.19 instead of 1.22. The effect on the $\ln S_u(f)$ profile in the MTS regime is very small for water at 300 K and 1.0 g cm⁻³. Earlier, the $1/f^\alpha$ region

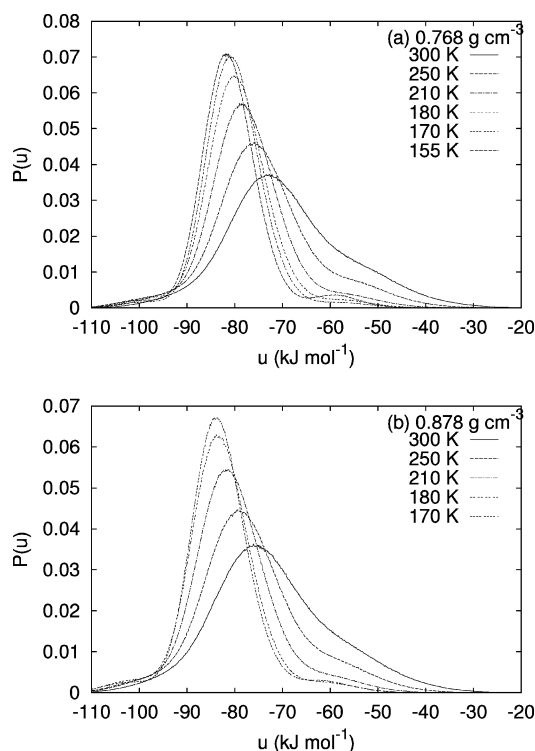


Figure 1. Static distribution, $P(u)$, of tagged potential energy, u , of methanol, along (a) 0.768 g cm⁻³ and (b) 0.878 g cm⁻³ isochores at different temperatures.

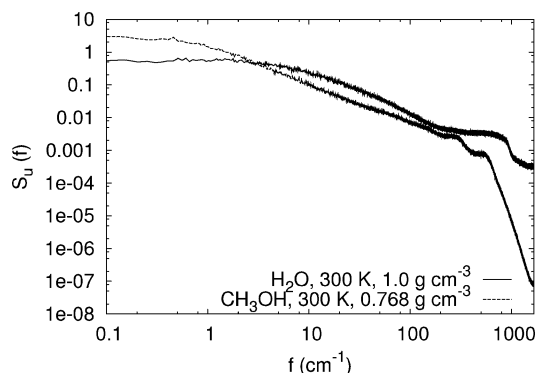


Figure 2. Comparison of power spectra associated with temporal fluctuations in tagged particle potential energy, $S_u(f)$, between methanol (H1 potential) and water (SPC/E potential) at 300 K. The densities of methanol and water were taken as 0.768 and 1 g cm⁻³, corresponding to experimental densities at 1 atm pressure.

extended from 1 to 200 cm⁻¹ with $\alpha = 1.4$, but now, the crossover shifts to higher frequencies and the MTS regime exists in the 8–200 cm⁻¹ range, with α being almost the same, i.e., 1.41. Since the changes in the $S_u(f)$ spectra will be similar for Figures 5, 6, and 7a in the original paper, we do not reproduce the corrected version of these figures here; details are available in ref 3.

Figure 8 of the original paper remains unchanged. The original paper had demonstrated (Figure 9) that a strong positive correlation exists between the diffusivity coefficient, D , and the

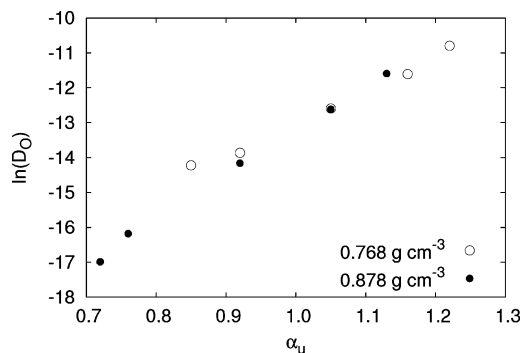


Figure 3. Correlation plot between the self-diffusion coefficient of oxygen and the scaling exponent, α_u , of the multiple time scale region of the $S_u(f)$ power spectra in methanol. Diffusivities are in units of $\text{cm}^2 \text{s}^{-1}$.

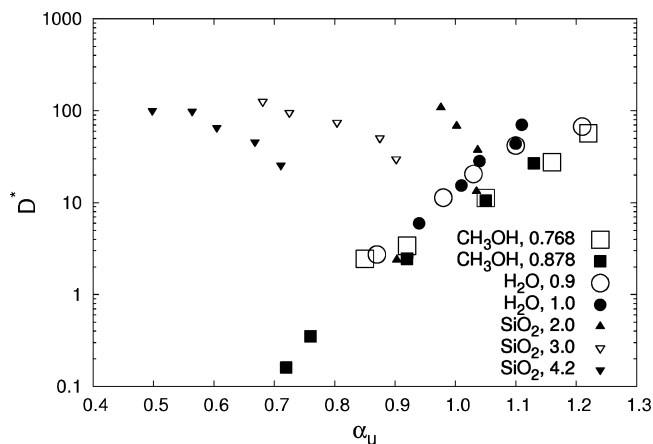


Figure 4. Correlation plot between the self-diffusion coefficient of oxygen in methanol and water and silicon ion in silica with the scaling exponent, α_u , of the multiple time scale region of the $S_u(f)$ power spectra. Dimensionless diffusivities, $D^* = D\rho^{1/3}/(k_B T/m)^{1/2}$, where ρ and m correspond to the number density and masses of the formula units, have been used to facilitate comparison between the different systems. The temperatures studied for water are 230, 250, 260, 280, and 300 K, and those for silica are in the range 4000–6000 K in steps of 500 K.

scaling exponent, α_u . Figure 3 replaces Figure 9 of the original paper. Figure 3 shows that the strong correlation still remains, though the α_u values change slightly.

Figure 10 of the original paper, which compared water, silica, and methanol in terms of D versus α_u correlation, is now replaced by Figure 4. The error in the computation of tagged particle potential energies also affected our earlier results for silica and water,^{2,4,5} and we have therefore recomputed the

scaling exponent of the multiple time scale region for these systems.^{3,6} The two molecular liquids (CH_3OH and H_2O) span almost the same range of α_u values and show a strong positive correlation between D and α_u . In contrast, the SiO_2 melt shows much lower values of α_u . The correlation is very similar in the case of hydrogen bonded molecular systems, water and methanol, but in the case of silica, this positive correlation is lost, though there is a slight negative correlation.

Correction of our error introduces only minor changes in the power spectral features of methanol in that the white noise crossover occurs at slightly higher frequencies and the scaling exponent, α_u , of the multiple time scale regime changes. The frequencies of local resonances are unchanged. The major change as a result of correcting our error is in the shape of the static distributions of the tagged potential energy of methanol molecules. The multimodality, observed earlier, was an artifact due to the error, which on correction is replaced by unimodal distributions but with significant deviations from Gaussian behavior, including the emergence of a second peak at low temperatures.

References and Notes

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Correction to the Cover Information for the Pierre-Gilles de Gennes Memorial Issue

Page 6A. A citation to an image on the cover for the Pierre-Gilles de Gennes Memorial Issue was added to the “On the cover” caption. The new caption reads “Liquid crystals are beautiful and mysterious; I am fond of them for both reasons. P.-G. de Gennes. Liquid crystal images courtesy of Professor Pawel Pieranski.” The caption was reposted on the Web on May 5, 2009. The new caption can be accessed at <http://pubs.acs.org/toc/jpcbfk/113/12>.

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