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Supplementary materials : Orientational dynamics in supercooled glycerol computed from MD simulations: self and cross contributions

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I. FORCE FIELD FOR GLYCEROL

The force field used in this work is the one initially introduced by Chelli *et al.* [1, 2], later optimized by Blieck *et al.* [3] and used since with only little differences by Egorov *et al.* [4], Busselez *et al.* [5] and Becher *et al.* [6]. The partial charges used for the glycerol molecules are shown in fig. S5. The harmonic bound, harmonic angle, and periodic torsion forces parameters are given in table S1, S2 and S3 respectively. The Lennard-Jones parameters are given in table S4.

II. SIMULATION RUNS

The simulation runs used in this work are described in table S5. At each temperature $T < 323\ K$, the equilibration is performed starting from the equilibrated state at $T + 10$ K.

III. EFFECT OF THE SIMULATION BOX SIZE

The effect of the simulation box size was studied by performing an additional simulation run at 323 K for only $N = 540$ molecules (7560 atoms) in a cubic cell of side length $a \approx 41$ Å. The dipole density $n(r)$ and the integrated cross-correlation contribution $\int_0^r c_1(r', t = 0)\mathrm{d}r$ are shown in fig. S1 for this case as well as for the box size used in the main text ($N = 2160$, $a \approx 65$ Å) at the same temperature. Both datasets display a similar behavior regarding cross-correlations: a first plateau is reached at $r \approx 8$ Å followed by an increase with a maximum slope reached at $r = a/2$. This box-size dependent second regime is due to the effect of PBCs on the treatment of electrostatic interactions with the PME method [7–9]. Using $N = 2160$ allows us to safely decouple the PCBs artifact from the physically meaningful behavior at $r < 15$ Å.

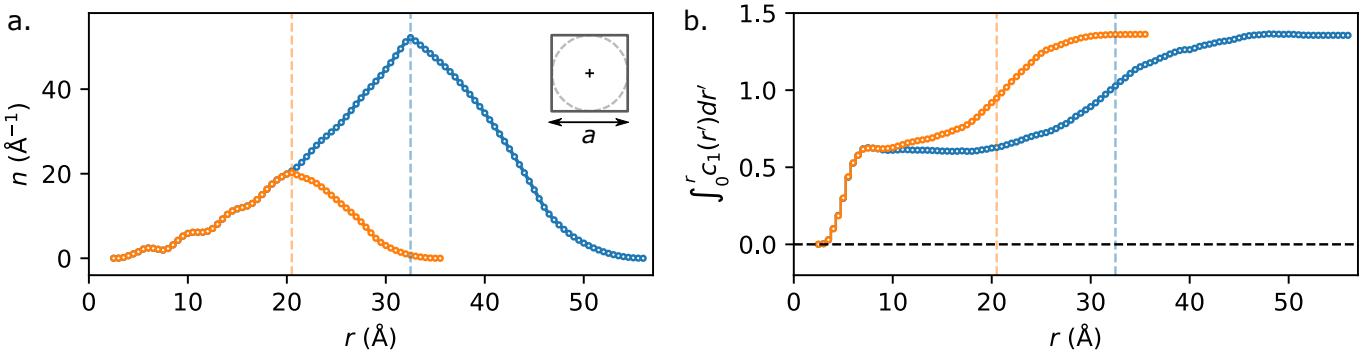

Figure S1. Effect of the simulation box size at $T = 323$ K $N = 2160$ molecules used in this study (blue) and $N = 540$ (orange). (a) Dipole density $n(t)$. The vertical dashed lines correspond to the half side $a/2$ of the simulation box. (b) Integrated cross-correlation $\int_0^r c_1(r', t = 0)\mathrm{d}r$.

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Table S1. Harmonic bond force parameters. The potential is of the form $E_\mathrm{b} = k_\mathrm{b}(r - r_0)^2$.

bond	k_b (kcal·mol^{-1}·Å^{-2})	r_0 (Å)
CC	310	1.526
CO	320	1.410
CH	rigid bond	1.090
OH	rigid bond	0.960

IV. CORRELATION FUNCTION

The correlation functions shown in fig. 1 and 4 of the main text are reproduced in fig. S2 and S2 with a logarithmic vertical axis in order to make the long time behaviour more visible.

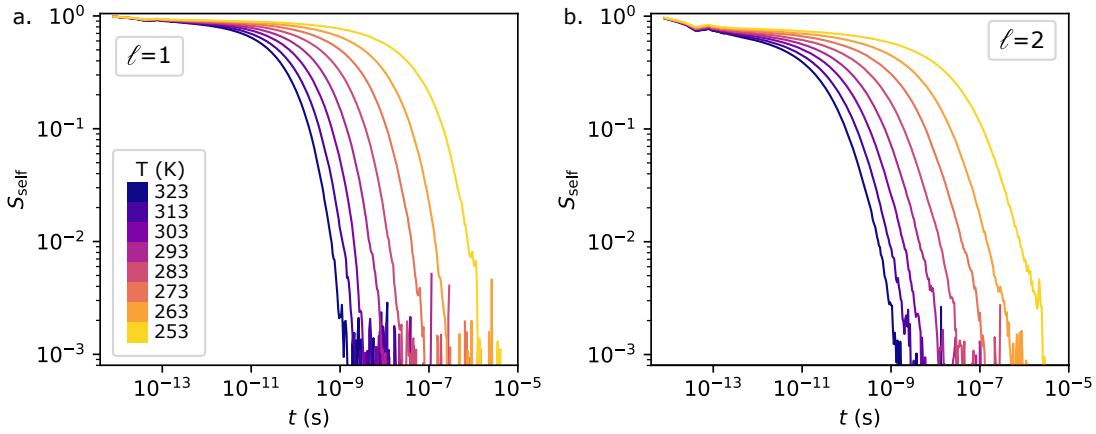

Figure S2. Dipole self correlation function (from fig. 1a of the main text) plotted with a logarithmic vertical axis.

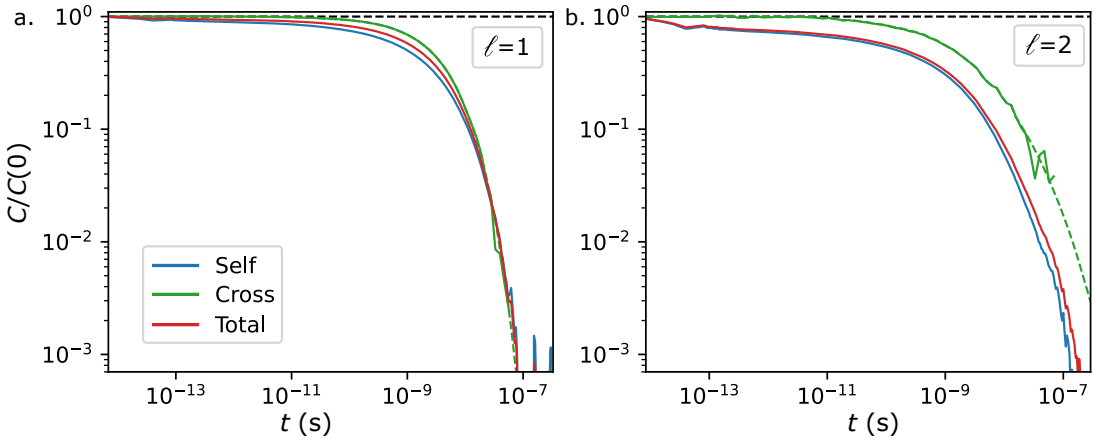

Figure S3. Correlation functions at $T = 273$ K (from fig. 4a-b of the main text) plotted with a logarithmic vertical axis. The dashed green line is an exponential fit on the long time part of the cross correlation function used to obtain the total correlation function $S_\mathrm{tot} = S_\mathrm{self} + S_\mathrm{cross}$.

V. COMPARISON OF $\mu^2 g_\mathrm{K}$ WITH EXPERIMENTS

Fig. S4 shows $\mu^2 g_\mathrm{K}$ obtained from the MD simulation in this work (red) and from experimental measurements of $\epsilon(0)$ and eq. 1 of the main text by Gabriel *et al.* [10].

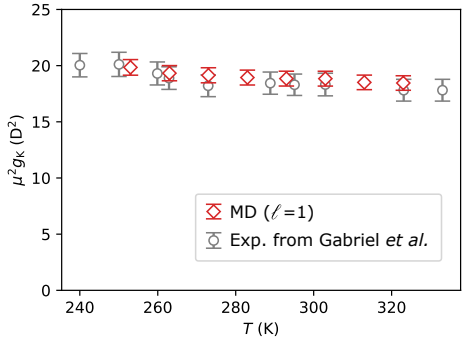

Figure S4. Temperature dependence of $\mu^2 g_K$ obtained from the MD simulation and experimentally from the measurement of the dielectric strength (from ref. [10]).

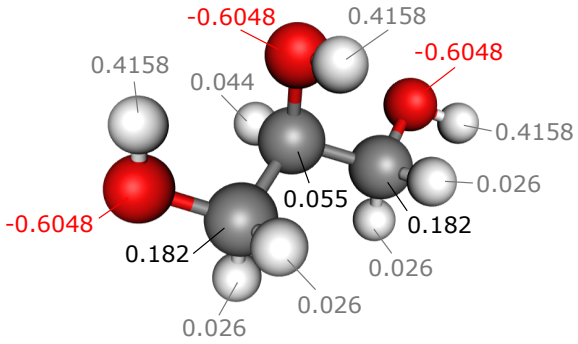

Figure S5. Atomic charges of the glycerol molecule.

Table S2. Harmonic angle force parameters. The potential is of the form $E_\theta = k_\theta(\theta - \theta_0)^2$.

angle	k_θ (kcal·mol^{-1}·rad^{-2})	θ_0 (°)
CCC	40	109.5
CCO	50	109.5
CCH	50	109.5
COH	55	108.5
HCH	35	109.5
OCH	50	109.5

Table S3. Periodic torsion force parameters. The potential is of the form $E_\Phi = k_\Phi(1 + \cos(n\Phi))$.

dihedral	V_n (kcal·mol^{-1})	n
CCCH	0.1556	3
CCCO	0.1556	3
OCCO	0.1440	3
OCCO	1.0000	2
OCCH	0.1556	3
HOCC	0.1667	3
HOCH	0.1667	3
HCCH	0.1556	3

Table S4. Lennard-Jones parameters. The potential is of the form $V_{LJ} = 4\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$. The input parameters of the Amber .frcmod file is the half atom-atom distance at which the potential reaches its minimum ($R_m = 2^{1/6}\sigma$).

atom	$R_m/2$ (Å)	σ (Å)	ϵ (kcal·mol^{-1})
C	2.1416	3.816	0.1094
O	1.6000	2.850	0.1591
aliphatic H	1.5569	2.774	0.0157
hydroxyl H	0.800	1.425	0.0498

Table S5. Details on the simulation runs.

T (K)	equil. steps	in τ_{self} unit.	in s	run steps	in τ_{self} unit.	in s
323	4×10^6	213	16 ns	3.5×10^6	186	14 ns
313	7×10^6	225	28 ns	7×10^6	225	28 ns
303	14×10^6	253	56 ns	14×10^6	253	56 ns
293	33×10^6	262	130 ns	30×10^6	238	120 ns
283	38×10^6	114	150 ns	75×10^6	225	300 ns
273	108×10^6	113	430 ns	215×10^6	226	430 ns
263	358×10^6	98	1.4 µs	710×10^6	194	2.8 µs
253	1830×10^6	101	7.3 µs	1210×10^6	67	4.8 µs

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