Supplementary Information Probing the Triplet Correlation Function in Liquid Water by Experiments and Molecular Simulations

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1 Relation between pressure derivative of pair correlation function with triplet correlation function

Herein we provide step-wise derivation of the relation between pressure derivative of pair correlation function with triplet correlation function presented in the main article. As shown in the main text of the article that for a system of N particles with positions given by 3N-dimensional vector \mathbf{r}^N , the pair and triplet density functions are related as:¹⁻⁴

$$\int \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r_3} = (N-2)\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2),$$
(S1)

where $\rho_N^{(3)}$ and $\rho_N^{(2)}$ are the triplet and pair density functions, respectively.

As the change in external pressure leads to a change in number of atoms in a given volume, to discuss these changes we should consider the problem in the grand canonical ensemble. We can rewrite the above equation as

$$\int \langle \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle \mathrm{d}\mathbf{r}_3 + 2 \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \langle N \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle \tag{S2}$$

where $\langle \cdots \rangle$ denotes the averages over the distribution of molecules in a given volume V. As in the real scenario $\langle N \rangle \to \infty$, the above equation becomes indeterminate and therefore it is rewritten as

$$\int \left[\langle \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle - \rho \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle \right] d\mathbf{r}_3 + 2 \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \langle N \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle - \langle N \rangle \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
(S3)

where ρ is the number density represented by $\rho = \langle N \rangle / V$. The right hand side of the above equation can be calculated from the fluctuation in the product of number of atoms with the pair density function and is readily expressed in terms of activity, $z = \frac{1}{\Lambda^3} \exp(\beta \mu)$, and differentiation of pair density function with respect to the activity (z)

$$z \frac{\partial \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle}{\partial z} = \langle N \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle - \langle N \rangle \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
(S4)

where, $\Lambda = h/\sqrt{2\pi m k_B T}$, is the thermal de Broglie wavelength and μ is the chemical potential.

The above relation can be established by the following way: In the grand canonical ensemble, if p(N) is the probability that at equilibrium a system of the ensemble contains precisely Nparticles irrespective of their coordinates and momenta and Ξ is the grand-canonical partition function, then n-particle density is defined in terms of its canonical ensemble counterparts as the sum⁴

$$\langle \rho_N^{(n)}(\mathbf{r}^n) \rangle = \sum_{N \ge n}^{\infty} p(N) \rho_N^{(n)}(\mathbf{r}^n)$$
 (S5)

$$= \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{z^N}{(N-n)!} \int \exp(-\beta U_N(\mathbf{r}^n)) d\mathbf{r}^{(N-n)}$$
(S6)

So the two-particle density in the grand-canonical ensemble can be written as

$$\langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{1}{\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int \exp(-\beta U_N(\mathbf{r}^n)) d\mathbf{r}^{(N-2)}$$
 (S7)

Now if we differentiate it with respect to z and multiply with z

$$z \frac{\partial \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle}{\partial z} = \frac{1}{\Xi} \sum_{N=2}^{\infty} N \frac{z^N}{(N-2)!} \int \exp(-\beta U_N(\mathbf{r}^n)) d\mathbf{r}^{(N-2)} -\frac{1}{\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int \exp(-\beta U_N(\mathbf{r}^n)) d\mathbf{r}^{(N-2)} \times \frac{\partial \ln \Xi}{\partial \ln z}$$
(S8)
$$= \langle N \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle - \langle N \rangle \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle,$$
(S9)

as in the grand canonical ensemble it has been proved that the average number of particle in the system is^4

$$\langle N \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N = \frac{\partial \ln \Xi}{\partial \ln z}.$$
 (S10)

Use of the standard thermodynamic relationship $(\partial z/\partial P)_T = z/\rho k_B T$ leads to the equation

$$z\frac{\partial\langle\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\rangle}{\partial z} = z\left(\frac{\partial\langle\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\rangle}{\partial P}\right)_T \left(\frac{\partial P}{\partial z}\right)_T$$
(S11)

$$= \rho k_B T \left(\frac{\partial \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle}{\partial P} \right)_T.$$
(S12)

Combining Eqns. ((S3)), ((S4)) and ((S12)) we can express the pressure derivative

$$\rho k_B T \left(\frac{\partial \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle}{\partial P} \right)_T = \int \left\{ \langle \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle - \rho \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle \right\} d\mathbf{r}_3 + 2 \langle \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle.$$
(S13)

A more convenient way to write the above equations is to use the corresponding correlation functions instead of the density functions.⁴ For a homogeneous, isotropic fluid, the correlation functions can be written as a function of three relative distances, $r = |\mathbf{r}| = |\mathbf{r}_2 - \mathbf{r}_1|$, $s = |\mathbf{s}| =$ $|\mathbf{r}_3 - \mathbf{r}_1|$ and $t = |\mathbf{s} - \mathbf{r}|$. By the use of $\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho^3 g^{(3)}(r, s, t)$ and $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g^{(2)}(r)$,⁴ the above expression will be

$$\rho k_B T \left(\frac{\partial \rho^2 g^{(2)}(r)}{\partial P} \right)_T = \rho^3 \int \left\{ g^{(3)}(r,s,t) - g^{(2)}(r) \right\} \mathrm{d}\mathbf{s} + 2\rho^2 g^{(2)}(r).$$
(S14)

On differentiation of the left-hand side of the above equation,

$$\rho k_B T \left(\frac{\partial \rho^2 g^{(2)}(r)}{\partial P} \right)_T = 2\rho^2 k_B T g^{(2)}(r) \left(\frac{\partial \rho}{\partial P} \right)_T + \rho^3 k_B T \left(\frac{\partial g^{(2)}(r)}{\partial P} \right)_T, \tag{S15}$$

and putting it into the Eqn. ((S14)), we get the relation between pair and triplet correlation functions in the form⁵

$$\rho \int \left\{ g^{(3)}(r,s,t) - g^{(2)}(r) \right\} d\mathbf{s} + 2g^{(2)}(r) \left\{ 1 - k_B T \left(\frac{\partial \rho}{\partial P} \right)_T \right\} - \rho k_B T \left(\frac{\partial g^{(2)}(r)}{\partial P} \right)_T = 0,$$
(S16)

This is one of the most important relations in the theory of liquids originally derived by Schofield⁵ and later used by several other groups.

2 Comparison with the existing experimental literature data of liquid Neon on triplet correlation functions using molecular dynamics simulations

2.1 Molecular dynamics details of simulation of liquid neon

To reproduce the experimental results on triplet correlation function existed in the literature of liquid neon, we have performed molecular dynamics simulations taking 8192 particles in a cubic simulation box using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. Lennard-Jones interatomic potential with standard energy and length scale parameters for neon i.e. $\epsilon = 36.82$ K and $\sigma = 2.789$ Å were used in the liquid state. Molar mass of the particle was taken to be 20.1797 amu. All the simulations were carried out under isothermal isobaric ensemble (NPT) condition. The temperature (35.05 K) and pressure (21.4 atm, 79.0 atm and 140 atm) for which we have calculated structure factor and corresponding triplet function are taken from Ref. 6. To integrate the equation of motion in MD simulation, velocity-Verlet algorithm is used. The temperature and pressure were maintained using Nose-Hoover thermostat and barostat, with time constants of 0.5 ps and 1 ps, respectively. At each pressure, the systems were initially equilibrated for 10 ns and then production runs were carried out for 10 ns. During the production runs, the configurations were stored every 500 MD steps. Structure factor at the aforementioned state-points were calculated using FT method as well as direct method mentioned in the method section of the main article (see Eqns. (17) and (19)). Then full triplet function and its all components at different mean pressures, $P_m = (P_1 + P_2)/2$ (50.2 atm, 80.7 atm and 109.5 atm) were calculated using Eqns. (20)-(23) mentioned in the main article. To calculate the $H_2(q)$ component of the full triplet function, S(0) values were calculated from the values of isothermal compressibility (see Table S1) similar to the case of water we followed.

Table S1 The limiting value S(0) for $q \to 0$ for liquid neon at 35.05 K and different pressures in molecular dynamics simulation. The value of S(0) calculated from isothermal compressibility is denoted as $S(0)^{\kappa_T}$ (see Eqn. (28) in the main article) while from the direct method (see Eqn. (19) in the main article) is denoted by $S(0)^{Direct}$. In direct method, S(0) were calculated by extrapolating the corresponding structure factor from accessible q_{min} to the $q \to 0$ region. Number density at three different pressures are denoted by ρ_N .

Pressure(atm)	$ ho_N(N/\text{\AA}^3)$	$S(0)^{\kappa_T}$	$S(0)^{Direct}$
50.2	0.03465	0.104190	0.107922
80.7	0.03526	0.089458	0.098288
109.5	0.03578	0.081402	0.082971

The comparison to the existing literature results were performed to substantiate our method of calculations of $\tilde{H}(q)$ and its three components. To our knowledge, for liquid neon there are no molecular dynamics results about triplet correlation functions using Egelstaff's approach available, so we compared our MD simulation results the experimental data.



2.2 Three components of triplet function of neon at 50.2 atm

Figure S1 Comparison of all components $(H_1(q), H_2(q) \text{ and } H_3(q))$ of full triplet function $(\tilde{H}(q))$ calculated from molecular dynamics simulations with that of experimental results by Waseda *et al.*⁶ for neon at 35.05 K temperature and 50.2 atm pressure ((a), (b) & (c)). In part (d), contribution of three components of $\tilde{H}(q)$ for liquid neon obtained from MD simulation at the same temperature and pressure is compared.



2.3 Full triplet function of liquid neon at different pressure

Figure S2 Full triplet functions $(\tilde{H}(q))$ obtained in our MD simulations at 35.05 K temperature and at (a) 50.2, (b) 80.7 and (c) 109.5 atm pressure with the experimental data given in Ref. 6.





Figure S3 Change on peak and pre-peak intensity of O-O structure factor on application of pressure in (a) simulation using TIP4P/2005 water model and (b) experiment.

4 Three components of full triplet function $(\tilde{H}(q))$ in water at different pressure



Figure S4 Behavior of each component $(H_1(q), H_2(q) \text{ and } H_3(q))$ of full triplet function, $\tilde{H}(q)$ in water (TIP4P/2005 water model) at 298 K temperature and (a) 500.5 bar, (b) 1510 bar (c) 2519 bar and (d) 3319 bar pressure.

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