

Supporting Information for “Volume viscosity and ultrasonic relaxation of ethanol-water mixtures studied by molecular dynamics simulation”

Tsuyoshi Yamaguchi

Graduate School of Engineering, Nagoya University, Chikusa, Nagoya, 464–8603, Japan

Corresponding Author:

Tsuyoshi Yamaguchi: yamaguchi.tsuyoshi@material.nagoya-u.ac.jp

S1. COEFFICIENT OF δE IN EQ. (5)

We defined the adiabatic fluctuation of isotropic pressure, $\delta P'$, in eq. (5) of the main text as

$$\delta P'(t) = \delta P(t) - \frac{\langle \delta P \delta E \rangle}{\langle |\delta E|^2 \rangle} \delta E(t). \quad (\text{S1})$$

On the other hand, it is defined in other literatures as¹⁻³

$$\delta P'(t) = \delta P(t) - \frac{1}{V} \left(\frac{\partial P}{\partial \epsilon} \right)_{N,V} \delta E(t), \quad (\text{S2})$$

where $\epsilon \equiv E/V$ denotes the energy per unit volume. Hereafter we show the equivalence of these two expressions.

The correlation of fluctuation of a physical quantity with δE can be converted into the derivative of its average value with respect to temperature as

$$\langle \delta P \delta E \rangle = k_B T^2 \left(\frac{\partial \langle P \rangle}{\partial T} \right)_{N,V}, \quad (\text{S3})$$

$$\langle |\delta E|^2 \rangle = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}. \quad (\text{S4})$$

The combination of these two equations gives

$$\frac{\langle \delta P \delta E \rangle}{\langle |\delta E|^2 \rangle} = \left(\frac{\partial \langle P \rangle}{\partial \langle E \rangle} \right)_{N,V} = \frac{1}{V} \left(\frac{\partial P}{\partial \epsilon} \right)_{N,V}, \quad (\text{S5})$$

which equates Eqs. (S1) and (S2).

We described $\delta P'$ in the form of eq. (5) of the main text for two reasons. The first one is that it clearly indicates that the contribution of δE is projected out. The second one is computational. In the numerical calculation of $K(t)$, three time correlation functions, $\langle \delta P(0) \delta P(t) \rangle$, $\langle \delta P(0) \delta E(t) \rangle$ and $\langle \delta E(0) \delta E(t) \rangle$, are evaluated simultaneously. The coefficient of δE in eq. (5) is easily evaluated as the combination of their initial values, and $K(t)$ is then calculated as the linear combination of these three correlation functions.

S2. CONCENTRATION DEPENDENCE OF PRESSURE IN OUR NVT-ENSEMBLE SIMULATION

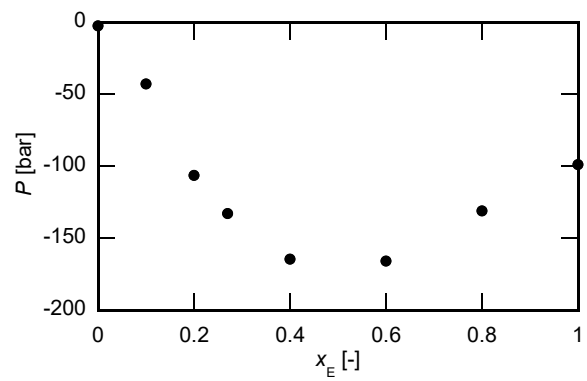


FIGURE S1. The mean pressure of our NVT-constant runs as the function of the mole fraction of ethanol, x_E .

S3. CONCENTRATION FLUCTUATION MODE

In the analysis of small angle X-ray or neutron scattering of binary liquid mixture, the low- q limiting value of the scattering function is often divided into the contributions of the fluctuation of the total number of molecules, N , and that of the concentration, c .^{4, 5} Denoting the indexes of the binary components as ‘E’ and ‘W’, these two quantities are related to the numbers of the component molecules as

$$N \equiv N_E + N_W, \quad (\text{S6})$$

$$c \equiv \frac{N_W}{N_E + N_W}. \quad (\text{S7})$$

The fluctuation of the former is related to the isobaric compressibility, whereas that of the latter is to the osmotic compressibility.

The linear fluctuation of eq. (S7) gives

$$\delta c = \frac{1}{N} [x_E \delta N_W - (1 - x_E) \delta N_E] = \frac{V}{N} [x_E \delta \rho_W - (1 - x_E) \delta \rho_E]. \quad (\text{S8})$$

The inner part of the square bracket of the right-hand side is equal to $\tilde{\rho}_c(\mathbf{q} = \mathbf{0})$ defined by eq. (14) of the main text. Therefore, our analysis based on $\tilde{\rho}_c(\mathbf{q})$ is essentially equivalent to the experimental analysis based on the concentration fluctuation.

References

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