Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information: Molecular dynamics study on helium nanobubbles in water

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1 The constant energy simulations

We performed the constant energy simulation after the constant temperature simulation for each of the nanobubble systems with bubble radii of about 2, 3, and 5 nm. Figure 1 shows the energy, temperature, and pressure during the constant energy simulation.

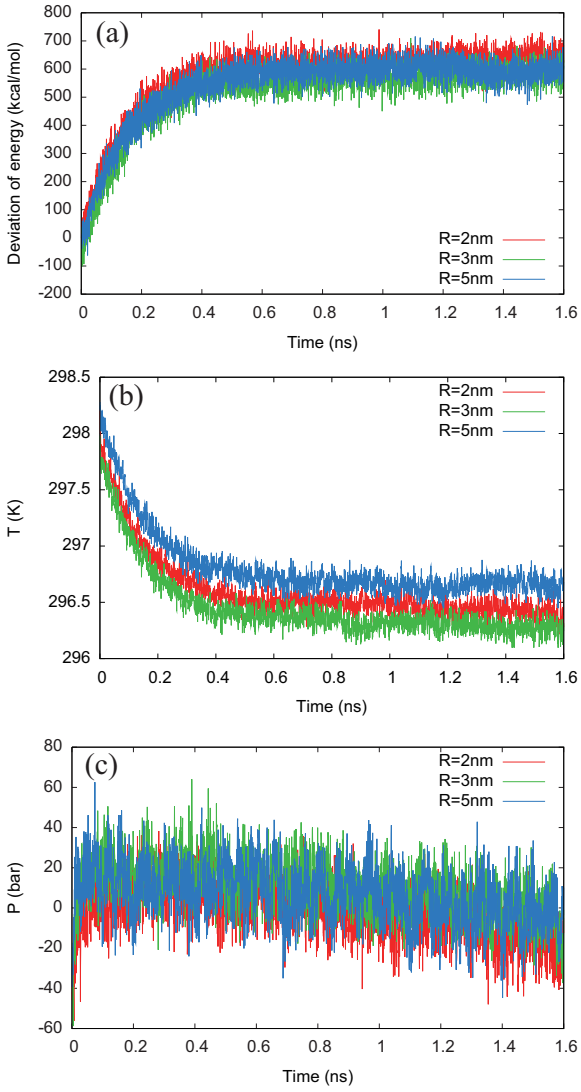

Figure 1: (a) The energy, (b) temperature, and (c) pressure of the nanobubble system during the constant energy simulation.

2 Computational details

We calculated the normal pressure profile of the nanobubbles using the Irving-Kirkwood method and the Thompson's algorithm. [1, 2] This algorithm can be used for the pair potential only. We decomposed the forces coming from the each angle term to two pair-forces, and used shifted Coulomb potential with the same cutoff as that of the Lennard-Jones potential. Figure 2 shows that the kinetic, bonded, and non-bonded contributions to the normal pressure profiles.

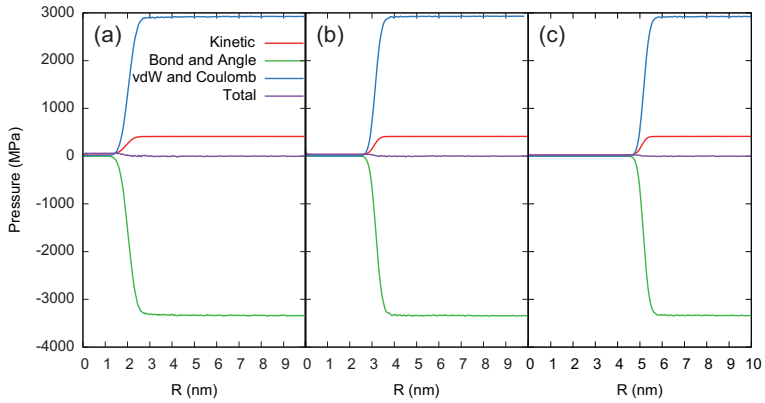

Figure 2: Components of pressure profile for the bubbles with the initial radii of (a) 2 nm, (b) 3 nm, and (c) 5 nm, respectively.

Surface tensions of bubble γ were calculated using the formula,

$$\gamma^3 = \frac{3}{8}(p_{\text{in}} - p_{\text{out}})^2 \int_0^{R_\infty} r^2 \left(P_{\text{N}}(r) - p_{\text{out}}\right) dr. \tag{1}$$

The p_{in} and p_{out} are the inner and outer pressures, respectively, which were determined by fitting the normal pressure profile $P_{\text{N}}(r)$ to the hyperbolic tangent function,

$$P(r) = \frac{p_{\text{in}} + p_{\text{out}}}{2} - \frac{p_{\text{in}} - p_{\text{out}}}{2} \tanh\left(2(r - R_p)/\xi_p\right). \tag{2}$$

R_∞ must be chosen as $P_{\text{N}}(r) = p_{\text{out}}$ for $r > R_\infty$. In practice, we used a R_∞ of 10 nm for all cases. The fitted parameters for the nanobubbles are shown in Table 1.

Table 1: R_{ini} is the initial radius of bubble. p_{in} and p_{out} are the inner and outer pressures, respectively. ξ_p is the interfacial width of pressure.

R_{ini} (nm)	2	3	5
p_{in} (MPa)	61.248	38.650	24.130
p_{out} (MPa)	-1.637	-0.762	-1.804
ξ_p (nm)	0.634	0.293	0.274

The surface of tension was calculated by the Laplace equation,

$$R_{\text{s}} = \frac{2\gamma}{p_{\text{in}} - p_{\text{out}}}, \tag{3}$$

with the determined surface tension γ.

We also calculated the surface tension for a flat water surface using

$$\gamma_\infty = \frac{L_z}{2}\left[\langle P_{zz}\rangle - \frac{1}{2}\left(\langle P_{xx}\rangle + \langle P_{yy}\rangle\right)\right], \tag{4}$$

where L_z is the cell length in z-direction, and $P_{\alpha\beta}$ is a component of the stress tensor. [3] The $\langle \ldots \rangle$ refer to time average.

3 Additional figures

Figure 3 shows the dipole and quadropole densities around the nanobubble interface. Figure 4 shows the electrostatic potential around the nanobubble interface and its dipole and quadropole contributions.

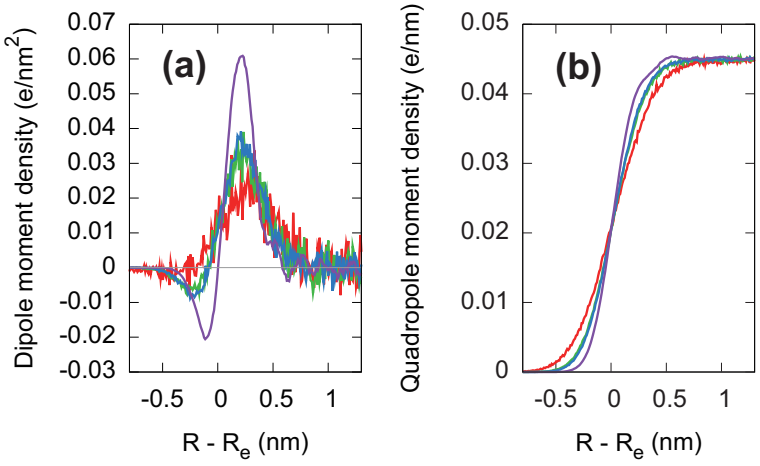

Figure 3: (a) Dipole and (b) quadropole moment densities for each of bubbles with the initial radii of 2 nm (red), 3 nm (green), and 5 nm (bule). Those for the flat water surface are also shown by violet lines.

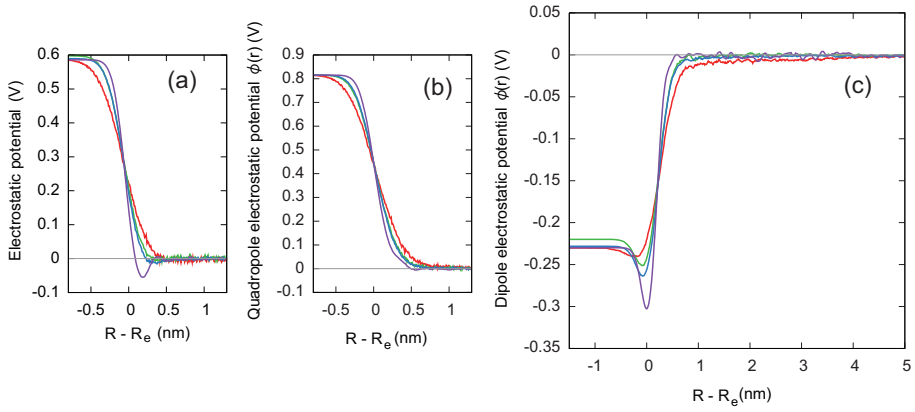

Figure 4: (a) Electrostatic potential and (b) its quadropole and (c) dipole contributions for each of bubbles with the initial radii of 2 nm (red), 3 nm (green), and 5 nm (bule). Those for the flat water surface are also shown by violet lines.

References

[1] J. H. Irving and John G. Kirkwood. The statistical mechanical theory of transport processes. iv. the equations of hydrodynamics. *J. Chem. Phys.*, 18:817–829, 1950.

[2] S. M. Thompson, K. E. Gubbins, J. P. R. B. Walton, R. A. R. Chantry, and J. S. Rowlinson. *J. Chem. Phys.*, 81:530–542, 1984.

[3] David Brown and Sylvie Neyertz. A general pressure tensor calculation for molecular dynamics simulations. *Mol. Phys.*, 84:577 – 595, 1995.