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.](image)

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 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 $\gamma$ were calculated using the formula,

$$\gamma^2 = \frac{3}{8} (p_{in} - p_{out})^2 \int_0^{R_{\infty}} r^2 (P_N(r) - p_{out}) \, dr.$$  \(\text{(1)}\)

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

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

$R_{\infty}$ must be chosen as $P_N(r) = p_{out}$ for $r > R_{\infty}$. In practice, we used a $R_{\infty}$ 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. $\xi_p$ is the interfacial width of pressure.

<table>
<thead>
<tr>
<th>$R_{ini}$ (nm)</th>
<th>2</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{in}$ (MPa)</td>
<td>61.248</td>
<td>38.650</td>
<td>24.130</td>
</tr>
<tr>
<td>$p_{out}$ (MPa)</td>
<td>-1.637</td>
<td>-0.762</td>
<td>-1.804</td>
</tr>
<tr>
<td>$\xi_p$ (nm)</td>
<td>0.634</td>
<td>0.293</td>
<td>0.274</td>
</tr>
</tbody>
</table>

The surface of tension was calculated by the Laplace equation,

$$R_s = \frac{2\gamma}{p_{in} - p_{out}},$$  \(\text{(3)}\)

with the determined surface tension $\gamma$.

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

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

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 (blue). 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 (blue). Those for the flat water surface are also shown by violet lines.

References
