Supporting Information for

Capillarity induced disassembly of virions in carbon nanotubes

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1.1 Numerical Calculation

In the initial capillary filling stage (figure 1S(a)), the outer surface of the cup-stacked-type CNT will be wet in advance, followed by the transient capillary filling of the CNT. The two tips of a CNT may be filled simultaneously, but more likely, non-simultaneously. Then, when the CNT is fully filled with the suspension and both its ends are still immersed in the surrounding suspension, the second “static” stage will occur and none influx of the suspension into the CNT is expected (figure 1S(b)). Later, because of the gradual evaporation of the suspension and the large length-to-radius ratio of the cup-stacked-type CNT (lengths up to 200 μm)[1], the suspension covering the CNT will retreat first from one end with the other still immersed in the surrounding suspension (figure 1S(c)). According to the study by Kim and co-authors [2], suspension may continuously enter the immersed end (steady state filling stage) because of the evaporation of water at the other end.

Figure 1S. Illustration of the three different stages after the virion suspension was loaded on a copper grid supporting the empty CNTs.

Therefore, it is possible for a CPMV virion to enter a CNT during the initial capillary filling stage or the later steady state filling process. The numerical calculations below were carried out on commercially available finite element method software (COMSOL 3.3a).
1.1.1 Filling CNTs with CPMV Virions in Later Steady State Filling Stage

To enable a detailed evaluation of the repulsive electrostatic and “attractive” hydrodynamic forces acting on a CPMV virion approaching a CNT in the later steady state filling stage (figure 1S(c)), the problem is simplified to that of a spherical virion moving along the axis of a like-charged cylindrical nanotube with a curved pore entrance and uniform wall thickness (25 nm). Due to axial symmetry, we can model the electrostatic field and flow in two-dimensions (2-D) instead of three-dimensions (3-D). The figure 2S shows a sample modelling domain (grey).

**Figure 2S.** Typical symmetric modeling domain for the numerical calculation of electrostatic and hydrodynamic forces as a function of separation distance between a CPMV virion and the entrance of a CNT in the later steady state filling stage (figure 1S(c)).

1.1.1.1 Hydrodynamic Force

For the steady state influx at the immersed end induced by the evaporation of water at the other end, the Navier–Stokes equations for incompressible flow can be written as:

\[
\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot (\eta \nabla \mathbf{u}) + \mathbf{u} \cdot \nabla \mathbf{u} + \nabla p = 0 \quad (1)
\]

\[
\nabla \cdot \mathbf{u} = 0 \quad (2)
\]

Equation (1) is the momentum balance, and equation (2) is the equation of continuity for incompressible fluids.

The boundary conditions are given below:

- On AB, AC, and BH: \([-pI + \eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)]n = -P_o n\) (Pressure)
- n \cdot \mathbf{u} = 0
- On CE and FD: \(t \cdot [-pI + \eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)]n = 0\) (Symmetry)
- On EF, GH, and GI: \(\mathbf{u} = 0\) (No slip)[3]
- On DI: \(\mathbf{u} = u_o\) (Velocity)

The hydrodynamic force, which only has a \(Z\) component due to axial symmetry, can be obtained by integrating the stress tensor over the virion surface:

\[
F_H = 2\pi \int \mathbf{m} \cdot \left[-pI + \eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)\right] ds \quad (3)
\]

The variables and parameters appear:

- \(\rho\) density of water at 300 K (kg m\(^{-3}\))
1.1.1.2 Electrostatic Force

The zeta potential of the purified CNTs under neutral conditions (pH 7.0) was measured by Zetasizer 3000HS to be –27.6 mV, similar to that of the CPMV virion (about –25 mV). We assume the inner and outer surfaces of the nanotube have the same surface potential. The electrolyte is the phosphate buffer or the diluted phosphate buffer (10 mM or 0.1 mM). In electrostatic and thermodynamic equilibrium, the electric potential in the electrolyte solution obeys the nonlinear Poisson–Boltzmann equation:

$$-\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \psi) = \sigma$$  \hspace{1cm} (4)

To facilitate calculation, corresponding 2-D Poisson–Boltzmann equation can be normalized in cylindrical coordinates as:

$$\frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{R} \frac{\partial \Psi}{\partial R} + \frac{\partial^2 \Psi}{\partial Z^2} = -\frac{1}{2} \sum z_i \varepsilon_i \exp(-z_i \Psi)$$  \hspace{1cm} (5)

The dimensionless parameters and coordinates are defined as follows:

$$R = \kappa r; Z = \kappa Z; \Psi = \varepsilon_0 \varepsilon_r \kappa T$$

The boundary conditions are given below:

On AB, AC, CE, FD, DI, and HB \hspace{1cm} \( n \cdot \nabla \Psi = 0 \)

On EF \hspace{1cm} \( \Psi = \Psi_{\text{virion}} \)

On GH and GI \hspace{1cm} \( \Psi = \Psi_{\text{CNT}} \)

Because of axial symmetry, the electrostatic force will only have a \( Z \) component and can be directly calculated according to:

$$F_E = \varepsilon_0 \varepsilon_r \pi (\kappa a)^2 \left( \frac{kT}{e} \right)^2 \int_0^\pi |\nabla \Psi|^2 \cos \theta \sin \theta d\theta$$  \hspace{1cm} (7)

The variables and parameters appear:

- \( \varepsilon_0 \) permittivity of vacuum (8.854 x 10^{-12} F m^{-1})
- \( \varepsilon_r \) relative permittivity (F m^{-1})
- \( \Psi \) electric potential (V)
- \( \sigma \) space charge density (C m^{-2})
- \( \Phi \) reduced potential
- \( R \) dimensionless coordinates (\( R = \kappa r \))
1.1.2 Capillary Filling of CNTs

To explore the reasons for the disassembly of virions during the initial capillary filling of CNTs, we simulated the initial transient capillary filling of a cylindrical nanotube with one end deeply immersed in surrounding water, and Level Set Two-Phase Flow application mode was used. Due to axial symmetry, the flow in 3-D can be also reduced to 2-D. Figure 3S below shows a typical modelling domain (grey).

![Figure 3S](image-url)

**Figure 3S.** An axisymmetric modelling domain for the initial transient capillary filling of nanotube (inner diameter of 50 nm).
Since the nanotube is horizontally placed with the channel initially filled by air, the Level Set Two-Phase Flow application mode neglecting the gravity force was used:

\[
\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho \mathbf{u} \cdot \nabla \mathbf{u} + \nabla p = F_{st} + F_{fr}
\]

\[
\nabla \cdot \mathbf{u} = 0
\]

(8)

\[
\frac{\partial \phi}{\partial t} + \nabla \phi \cdot \mathbf{u} = \gamma \nabla \cdot \left( \epsilon \nabla \phi - \phi (1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right)
\]

Where \( \phi \) is the level set function (that is, the volume fraction of water). Air corresponds to \( \phi < 0.5 \), and water corresponds to \( \phi > 0.5 \). The density and the dynamic viscosity are functions of \( \phi \) according to:

\[
\rho = \rho_{\text{air}} + (\rho_{\text{water}} - \rho_{\text{air}})\phi
\]

(9)

\[
\eta = \eta_{\text{air}} + (\eta_{\text{water}} - \eta_{\text{air}})\phi
\]

(10)

The interface normal is calculated from:

\[
\mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|}
\]

(11)

Normally, the surface tension force is:

\[
F_{st} = \sigma \kappa \mathbf{n}
\]

(12)

Because \( \kappa \) depends on second derivatives of the level set function \( \phi \), leading to poor accuracy of the surface tension force, alternative formulation is used:

\[
F_{st} = \nabla \cdot (\sigma (1 - (\mathbf{n} \cdot \mathbf{n})^T)) \delta)
\]

(13)

The \( \delta \) function is approximated by a smooth function according to:

\[
\delta = 6 |\nabla \phi| \phi (1 - \phi)
\]

(14)

The frictional (or shear) force is given below[4]:

\[
F_{fr} = -\frac{\eta}{\beta} \mathbf{u}
\]

(15)

The boundary conditions are given below:

On AB, AF, and BD
\[
[-pI + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \mathbf{n} = -p_0 \mathbf{n}
\]

(Pressure)

\( \phi = 1 \)

\( \mathbf{n} \cdot \mathbf{u} = 0 \)

On GF and GH
\[
t \cdot [-pI + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \mathbf{n} = 0
\]

(Wet wall)

\( F_{fr} = -(\eta / \beta) \mathbf{u} \)

\( \mathbf{n} \cdot \mathbf{n}_{\text{interface}} = \cos(\theta) \)

\( \mathbf{t} \cdot \mathbf{u} = 0 \)

On HC
\[
\mathbf{n} \cdot [-pI + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \mathbf{n} = -p_0
\]

(Normal flow, pressure)

On CE and ED
\[
\mathbf{r} = 0
\]

(Axial symmetry)

On EG
\[
[-pI + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \mathbf{n} = 0
\]

(Initial air–water interface)

Initially, the velocities of water and air are zero, and the space surrounding the channel is filled with water, whereas the channel is filled with air, that is:

\( \phi = 1 \) in ABDEGF subdomain

\( \phi = 0 \) in CEGH subdomain
The variables and parameters appear:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho )</td>
<td>density of fluid at ((\text{kg m}^{-3}))</td>
</tr>
<tr>
<td>( u )</td>
<td>velocity field ((\text{m s}^{-1}))</td>
</tr>
<tr>
<td>( t )</td>
<td>time ((\text{s}))</td>
</tr>
<tr>
<td>( \eta )</td>
<td>dynamic viscosity of fluid ((\text{Pa s}))</td>
</tr>
<tr>
<td>( \tau )</td>
<td>transpose</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure ((\text{Pa}))</td>
</tr>
<tr>
<td>( p_0 )</td>
<td>environmental pressure ((1 \times 10^5 \text{ Pa}))</td>
</tr>
<tr>
<td>( F_{st} )</td>
<td>surface tension force ((\text{N}))</td>
</tr>
<tr>
<td>( F_{fr} )</td>
<td>frictional (or shear) force on walls ((\text{N}))</td>
</tr>
<tr>
<td>( \phi )</td>
<td>level set function</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>reinitialization parameter ((1 \text{ m s}^{-1} \text{ was used in this study}))</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>parameter controlling interface thickness with a default value equal to the largest value of the mesh size used in this study ((\text{m}))</td>
</tr>
<tr>
<td>( \rho_{\text{air}} )</td>
<td>density of air at 300 K ((\text{kg m}^{-3}))</td>
</tr>
<tr>
<td>( \rho_{\text{water}} )</td>
<td>density of water at 300 K ((\text{kg m}^{-3}))</td>
</tr>
<tr>
<td>( \eta_{\text{air}} )</td>
<td>dynamic viscosity of air at 300 K ((\text{Pa s}))</td>
</tr>
<tr>
<td>( \eta_{\text{water}} )</td>
<td>dynamic viscosity of water at 300 K ((\text{Pa s}))</td>
</tr>
<tr>
<td>( n )</td>
<td>normal vector</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>surface tension coefficient of water ((0.073 \text{ N m}^{-1}))</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>curvature of the air–water interface</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Dirac delta function</td>
</tr>
<tr>
<td>( \beta )</td>
<td>slip length of the channel ((\text{m}) [5])</td>
</tr>
<tr>
<td>( \theta )</td>
<td>equilibrium contact angle ((\text{a value of } \pi /6 \text{ was estimated from figure 1(c)}))</td>
</tr>
</tbody>
</table>
1.2. Supporting Figures

Figure 4S. Molecular graphics images of the CPMV capsid and its asymmetric protein unit. The images were produced by using the UCSF Chimera package from the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco.

Figure 5S. Typical HRTEM images of a purified cup-stacked-type CNT (left) and its sidewall (right). The scale bars at left and right are 50 and 10 nm, respectively.
1.3. Further Discussion About the Nanobubbles

According to the homogeneous nucleation theory (in pure liquid) [6], the tensile strength is as large as $2S/R$ (where $S$ is the surface tension of water, and $R$ is the radius of a void in water). In our case, however, the nucleation occurs at the boundary between the water and the solid wall. When rupture occurs at such sites, it is heterogeneous nucleation. According to the heterogeneous nucleation theory [6], the tensile strength could be zero in the limit as $\theta \rightarrow \pi$ (where $\theta$ is the contact angle of the solid surface with the liquid), because the tensile strength in this case is given by $2S \sin \theta / R$. Therefore, although the tensile strength for a completely wetting surface is comparable with that for homogeneous nucleation, the presence of an incompletely-wetting surface would cause heterogeneous nucleation and much reduced tensile strength [6]. Therefore, during the initial transient capillary filling process, the vapour seeds will automatically nucleate.
at the water–nanotube interface, and then larger nanobubbles will come from the growth and coalescence of these vapour seeds.

References in Supporting Information

[3] Due to interface interaction, fluid is pinned up on solid surface to some critical shear stress, beyond which it (partially) slips. Considering the velocity in this steady filling stage is low enough ($\times 10^{-5}$ m s$^{-1}$), the “No slip” boundary condition is reasonable and simplifies the numerical calculation.
[5] Significantly large slip lengths have been observed on various hydrophobic surfaces (such as common hydrophobic CNTs), whereas a relatively small slip length is suitable for a hydrophilic surface[7] (i.e., the cup-stacked-type CNTs here) because of stronger water–wall interaction. Therefore, only results with slip length of 10 nm were shown in this study, though a wide range of values (10–1000 nm) has been tested. It should be noted that a larger slip length can promote the capillary filling, but the results and conclusions presented in this study are not affected.