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Carbon Nanotubes as Thermally-Induced Water Pumps

Elton Oyarzua,[†] Jens Honore Walther,^{‡,¶} Constantine M Megaridis,[§] Petros Koumoutsakos,[¶] and Harvey A. Zambrano^{*,†}

[†]*Department of Chemical Engineering, Universidad de Concepcion, Concepcion, Chile*

[‡]*Department of Mechanical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

[¶]*Computational Science and Engineering Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, CH-8092 Zurich, Switzerland*

[§]*Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago IL, USA*

E-mail: harveyzambrano@udec.cl

Phone: +56 (0)41 2201468

Abstract

Thermal Brownian Motors (TBMs) are nanoscale machines that exploit thermal fluctuations to provide useful work. We introduce a TBM-based nanopump which enables continuous water flow through a Carbon Nanotube (CNT) by imposing an axial thermal gradient along its surface. We impose spatial asymmetry along the CNT by immobilizing certain points on its surface. We study the performance of this molecular motor using Molecular Dynamics (MD) Simulations. From the MD trajectories, we compute the net water flow and the induced velocity profiles for various

11 imposed thermal gradients. We find that spatial asymmetry modifies the
12 vibrational modes of the CNT induced by the thermal gradient, resulting
13 in a net water flow against the thermal gradient. Moreover, the kinetic
14 energy associated with the thermal oscillations rectifies the Brownian mo-
15 tion of the water molecules, driving the flow in a preferred direction. For
16 imposed thermal gradients of 0.5-3.3 K/nm, we observe continuous net flow
17 with average velocities up to 5 m/s inside CNTs with diameters of 0.94, 1.4
18 and 2.0 nm. The results indicate that the CNT-based asymmetric thermal
19 motor can provide a controllable and robust system for delivery of continu-
20 ous water flow with potential applications in integrated nanofluidic devices.

21 **Keywords**

22 Thermal pump, thermal vibrations, single-walled carbon nanotubes, nanofluidics, molecular
23 dynamics.

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27
28 Recent developments in nanotechnology are enabling the fabrication of devices such as
29 nano Lab-On-a-Chip (LOC) units.^{1,2} These integrated systems hold the promise of combin-
30 ing in a single nanochip and with molecular level resolution, the complete sequence of all
31 technical stages found in traditional clinical laboratories. Nanochannels are an essential part
32 of such systems, as conduits are needed to integrate the functional network components. The
33 development of nanoscale LOC (nLOC) units relies on the rational design of nanochannels
34 conducting the fluids and require a pumping mechanism for driving the flows. Flows in

35 nanoconfinement are known to behave differently than flows at the macro- and micro-scale
 36 due to dramatic increases of the surface-to-volume ratio. It has been reported that water
 37 transport through carbon nanotubes is one to five orders of magnitude faster than predicted
 38 by continuum models.³⁻⁵ In addition to inducing fast water flow, CNTs possess extraor-
 39 dinary mechanical, electronic, thermal and chemical properties,⁶ making them attractive
 40 candidates as conduits of nanofluidic devices. At the same time, the mechanisms required
 41 to drive water flow in nanoconfined geometries remain the subject of intense research.⁷ It
 42 has been reported that large pressure gradients are required to induce flow in CNT based
 43 nanomembranes,^{5,8} while electrokinetic flows rely on single-file transport of water molecules
 44 in a CNT⁹⁻¹¹ and capillarity is not a means to deliver continuous flow. Finally, due to the
 45 ultra smoothness of the CNT walls¹² and their high thermal conductivity,¹³ mass transport
 46 inside CNTs (as driven by imposed thermal gradients) has received considerable attention
 47 over the past decade.¹⁴⁻²⁵

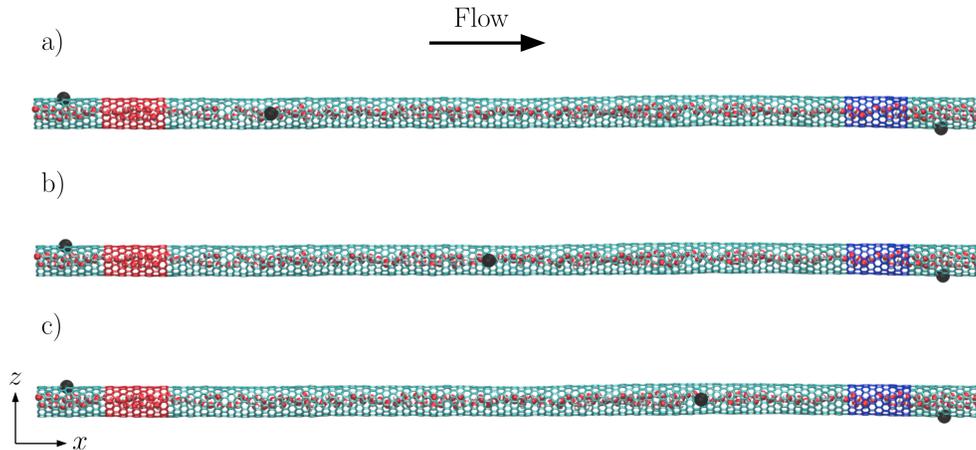


Figure 1: Illustration of the different CNT configurations studied in this work. The black spots indicate the fixed points along each CNT. The red and blue zones represent the heated sections of the CNT. The lengths of the CNTs were either 30nm or 60nm.

48 In this work, molecular dynamics (MD) simulations are employed to investigate the
 49 continuous flow of water inside a CNT, as driven by an imposed constant thermal gradient.
 50 We propose a nanomotor based on the thermal Brownian ratchet concept²⁶ to enable fast

51 and continuous water flow through a nanoconduit. The device consists of a single-wall CNT
52 filled with water. The CNT is fixed at three points, as shown in Figure 1, with the central
53 fixed point working as a pivot. Two heating zones near the ends impose a thermal gradient
54 along the CNT. The spatial symmetry of the system is broken by the specific position of the
55 fixed points, as depicted in Figure 1. The thermal excitation of the carbon atoms induces
56 oscillations along the CNT with peak amplitudes directly associated to the local temperature.
57 We find that differences in oscillation amplitudes between the higher and lower temperature
58 zones lead to a net water flow opposite to the thermal gradient (along declining temperature).
59 Using this configuration, we systematically investigate the flow dependence on the magnitude
60 of the imposed thermal gradient and the influence of the position of the central fixed point,
61 which breaks the symmetry of the system.

62 **Results and discussion**

63 We study first a reference case, which consists of a CNT with fixed points at its two ends and
64 its geometric center, as depicted in Figure 1b. The fixed carbon in the middle restricts the
65 position of the CNT without significantly altering the temperature profile along the CNT
66 (Supporting Information Fig. S3). Here, we use a 30 nm long zig-zag (12,0) CNT, completely
67 filled with water. The CNT is subjected to axial thermal gradients of either 1.6, 2.3 or
68 3.3 K/nm. Upon imposing a thermal gradient, we observe the water molecules inside the
69 CNT flow toward the low-temperature zone. Furthermore, by systematically increasing the
70 imposed thermal gradient, we note that the water axial velocity (likewise flow rate) increase
71 linearly, as shown in Figure 2a, with a rate following

$$v = -1.49\nabla T \quad (1)$$

72 which is consistent with prior studies of thermophoresis in CNTs.^{15–17}

73 The computed net water flow in the CNT is attributed to the thermal oscillations induced

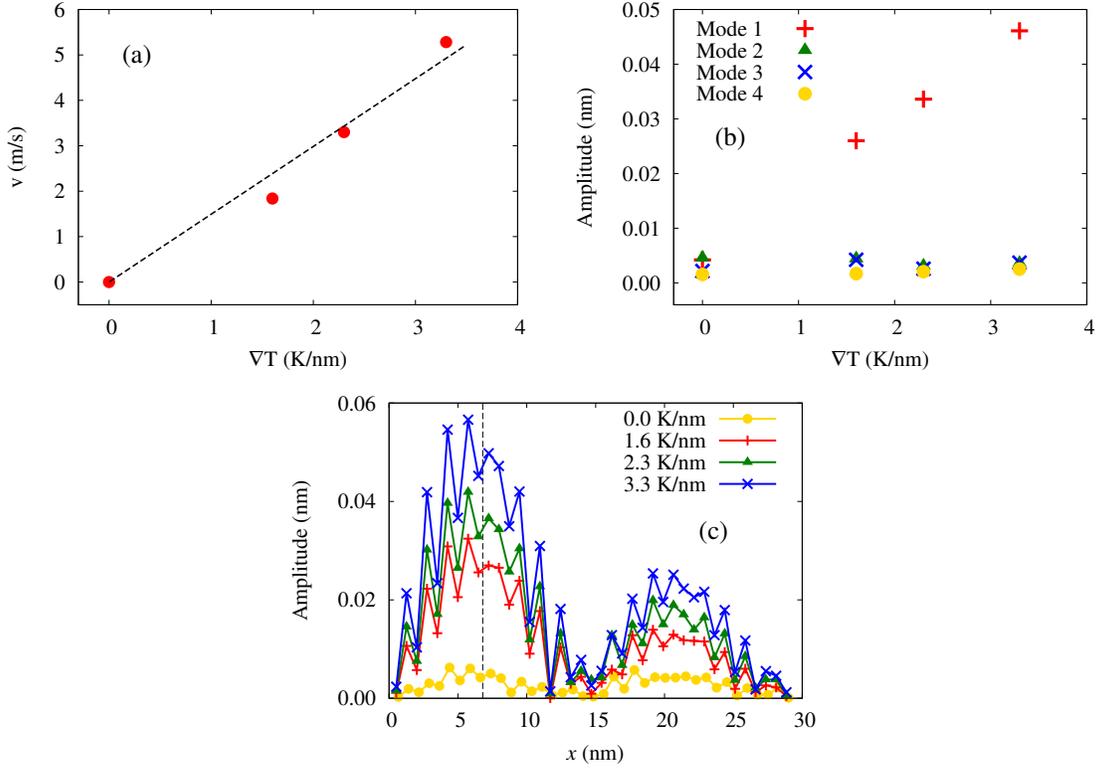


Figure 2: Mean velocities and FFT analysis for the 30 nm-long (12,0) CNT with fixed points as shown in Figure 1b. **(a)** Mean flow velocities of water for imposed thermal gradients of 0, 1.6, 2.3 and 3.3 K/nm. The dashed line corresponds to a linear fit of the data, under the condition $v_{(\nabla T=0)} = 0$ m/s. **(b)** Amplitudes of the vibrational modes 1–4 computed at 7 nm from the left end of the CNT. This position is depicted by the vertical dashed line in Figure 2c. **(c)** Amplitudes measured for the first mode at three different imposed thermal gradients along the axial direction of the CNT. The zero thermal gradient case (330 K) is also shown in this figure.

74 in the CNT according to the imposed thermal gradient. We find that the particular position
75 of the central fixed point is key to rectify the water motion in a preferential direction,
76 which results in a constant net flow of water. In order to quantify the oscillations of the
77 system, we perform a fast Fourier transform (FFT) analysis to determine the amplitudes
78 and frequencies of the thermally-induced vibrational modes of the CNTs. In particular, for
79 the system illustrated in Figure 1b, we perform the FFT analysis at a point located between
80 the left fixed point and the center point of the CNT, *i.e.* 7 nm from the left periodic border,
81 at different imposed thermal gradients. The amplitude values of the first four vibrational
82 modes as functions of the imposed thermal gradients are shown in Figure 2b. We note
83 that the frequencies of the vibrational modes are associated directly with the size of the
84 system, displaying no relation to the imposed thermal gradients. For example, for the
85 30 nm-long CNT filled with water, the first four vibrational modes have frequencies of 0.0925,
86 0.2100, 0.3750 and 0.4825 THz respectively. Figure 2b shows that an increase in the imposed
87 thermal gradient results in larger amplitudes in the vibrational mode 1. For modes 2, 3
88 and 4 no change is observed when different thermal gradients are imposed. Therefore, as a
89 thermal gradient is imposed, the induced flow rates depend on the amplitude of the thermal
90 oscillations exclusively in vibrational mode 1. Indeed, the amplitudes in vibrational mode
91 1 along the CNT for different imposed thermal gradients are shown in Figure 2c, which
92 shows that the high-temperature zone (left) acquires larger oscillations compared to the low-
93 temperature zone (right) for all imposed thermal gradients. Specifically, our results indicate
94 that the water flow in the CNT is induced by a continuous whip-like effect generated by the
95 difference in the oscillations of the CNT in the two heated zones. Moreover, as the imposed
96 thermal gradient is increased, the amplitude of the oscillations increases, inducing higher
97 flow rates.

98 Previous studies^{27,28} have shown that a net flow can be induced inside a CNT imposing
99 traveling waves. Hence, Insepov *et al.*²⁷ imposed Rayleigh traveling waves in a single-walled
100 CNT to transport gas. They observed a time-dependent flow rate with time decay. Likewise,

101 Qiu *et al.*²⁸ noted that by applying a periodic force in a cantilever CNT, a water net flow
102 was produced. Moreover, at higher applied forces, greater amplitudes at the free end of the
103 CNT were observed, leading to higher water flow rates. In terms of performance, our TBM
104 converts thermal energy directly into water flow with an efficiency of *ca.* 0.2%, similar to
105 the nanopump proposed by Qiu *et al.*²⁸ or the nanomotor studied by Hou *et al.*¹⁹ In gen-
106 eral, the TBM presented here works with similar efficiency as previously-proposed Brownian
107 motors.^{29–31} The calculation details of the efficiency associated with our TBM/CNT pump
108 are described in the Supporting Information. Furthermore, we propose that the mechanism
109 reported in the present study corresponds to a thermally-rectified motion, as previously
110 observed by Becton and Wang,³² who showed that a graphene nanoribbon mounted on a
111 thermalized graphene sheet moved toward the low-temperature zone of the sheet. We infer
112 that the mechanism driving the ribbon on the graphene sheet was the thermally-induced
113 oscillations on the graphene sheet generated by the imposed temperature gradient.

114 In order to gain insight into the mechanism driving the water flow in the CNT and
115 investigate further the role of the fixed central point, we vary systematically its position
116 as shown in Figure 1. We also conduct simulations for 60 nm-long (12,0) CNTs filled with
117 water under an imposed thermal gradient of 2 K/nm and positions of the fixed middle point
118 as shown in Figure 1. Further details of the distances and dimensions used in each simulation
119 are provided in the Supporting Information. For the three different cases, velocity profiles
120 with radial position are shown in Figure 3a. The position of the fixed middle point only
121 slightly modifies the water flow rate. For example, for case (a) (configuration shown in
122 Figure 1a), a lower flow rate is observed. This confirms that the axial flow rate is not
123 exclusively thermal-gradient dependent; there is also strong dependence on the vibrational
124 behavior in the CNT. In order to quantify the vibrational modes for the different cases, a
125 FFT analysis was performed.

126 The amplitudes measured for the three cases and the vibrational modes in the CNT
127 are shown in Figure 3b, c and d. These figures show that the position of the middle point

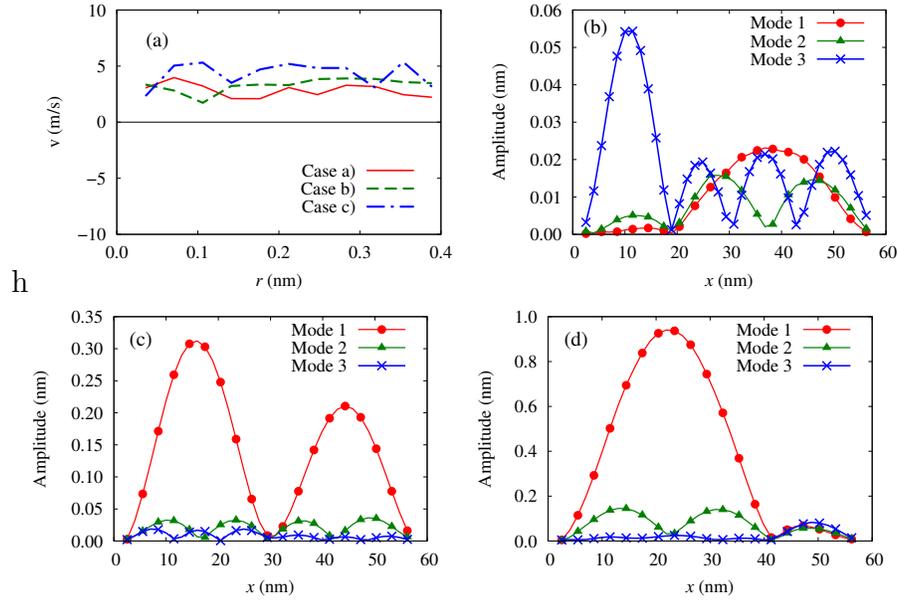


Figure 3: Velocity profiles and FFT analysis in a 60 nm-long (12,0) CNT with fixed points as shown in Figure 1a, b and c. All CNTs had an imposed thermal gradient of 2 K/nm. **(a)** Radial distribution of axial velocity for the three different cases of Figure 1 (case a, b, c respectively) with mean velocities of 2.8 m/s (red), 3.3 m/s (green) and 4.5 m/s (blue). **(b)** Amplitudes for vibrational modes 1–3 for CNT as shown in figure 1a (central fixed point at 1/3 of the length). **(c)** Amplitudes for vibrational modes 1–3 for CNT as shown in Figure 1b (central fixed point at half the length), and **(d)** Amplitudes for vibrational modes 1–3 for CNT as shown in Figure 1c (central fixed point at 2/3 of the length).

128 strongly affects the amplitudes of the first three vibrational modes under the same thermal
129 gradient. Considering the reference case, *i.e.*, the CNT with fixed end points and a fixed
130 point in the middle, the corresponding amplitudes of the three vibrational modes are shown
131 in Figure 3c. From this figure, we observe the same behavior as in Figure 2c, *i.e.*, a direct
132 impact of the thermal gradient on mode 1, with a greater amplitude in the high-temperature
133 zone compared to the low-temperature zone. On the other hand, mode 2 is not affected
134 by the imposed gradient, while mode 3 shows a slight increase in the amplitudes on the
135 high-temperature zone relative to the low-temperature zone. In the case with the lowest
136 flow rate measured, *i.e.* case (a), the amplitudes are presented in Figure 3b. This figure
137 shows how the vibrational modes of the CNT are distorted with respect to the case with
138 the central fixed point (Figure 3c); here the CNT acquires a greater freedom of movement
139 in the low-temperature zone, leading to an increase of the amplitude of mode 1 in this zone.
140 However, due to the particular direction of the flow, it follows that the third mode does drive
141 the fluid. In fact, the effect of mode 3 on driving the fluid is the most significant when the
142 CNT is restricted at 1/3 of its length. Here, the frequency of mode 3 is 0.065 THz, which
143 is more than four times the frequency of mode 1 (0.015 THz), leading to oscillations with a
144 higher frequency and amplitude in the high-temperature zone as compared to the oscillations
145 in the low-temperature zone. Finally, the amplitudes measured in the case with higher flow
146 rate, *i.e.* case (c), are depicted in Figure 3d. This figure shows how the amplitude of mode 1
147 is strongly increased, more than twice compared to the peak amplitude of the corresponding
148 mode in Figure 3c. Similar to Figure 3b, modes 2 and 3 are distorted by modifying the
149 central fixed point, leading to a greater amplitude in the high-temperature zone for mode
150 2, and in the low-temperature zone for mode 3. The results for the three cases, indicate
151 that the water flow is driven by an association between the frequencies and amplitudes of
152 “activated” vibrational modes³³ due to the particular fixed position of the point between
153 the two ends. To confirm this driving mechanism, two additional cases of the 60 nm-long
154 (12,0) CNT were simulated, with restrictions at 1/4 and 1/5 of the length, respectively. In

155 both cases, a water flow with mean velocity of *ca.* 3.5 m/s was calculated. Moreover, in the
156 high-temperature zone, a higher amplitude of mode 4 was computed for the case restricted at
157 1/4 length, and similarly, a higher amplitude of mode 5 was computed in the case restricted
158 at 1/5 length (see Supporting Information; Fig. S7 and Fig. S8). This indicates that the
159 position of the pivotal fixed point with respect to the total length of the CNT determines the
160 magnified harmonic vibrational mode driving the flow. Similar to the mechanism proposed
161 by Qiu *et al.*,²⁸ we infer that an axial centrifugal force is propelling the water molecules. In
162 our device, the magnitude of the centrifugal force is a consequence of the amplitudes and
163 the frequency of a specific vibrational mode induced by the imposed thermal gradient and
164 the particular position of the fixed middle point.

165 The feasibility of inducing continuous water flow in a CNT by imposing an external
166 temperature gradient has not been widely investigated. In a recent study, Zhao and Wu¹⁸
167 showed that by keeping two reservoirs at different temperatures and connecting them with
168 short aligned carbon nanotubes, net flow of water towards the low-temperature reservoir
169 was observed. They reported significant higher flow rates for longer CNTs connecting the
170 reservoirs, while keeping the end-to-end temperature difference constant (*i.e.* lower tem-
171 perature gradient). This disagrees with the present results, since we compute lower flow
172 rates for longer CNTs subjected to the same temperature difference (Supporting Informa-
173 tion Fig. S8). This discrepancy is mainly related to the different treatment of the carbon
174 atoms in the simulations, while Zhao and Wu¹⁸ imposed a harmonic restraining force to
175 all the carbon atoms in the nanotube, in the present study, the nanotube vibrations are
176 controlled without suppressing substantially the thermal oscillations of the nanotube. Ad-
177 ditionally, the finite length of the CNT membrane in the study of Zhao and Wu¹⁸ leads to a
178 higher energy barrier at the entrance, which is not taken into account in the present study.

179 To further explore this TBM, we evaluated the thermal pumping for CNTs with different
180 diameters. Simulations of water in CNTs with diameters of 1.4 nm and 2.0 nm, chirality
181 vectors (18,0) and (26,0) respectively, were conducted. In both systems, a fixed thermal

182 gradient of 3 K/nm was imposed along the CNTs. Water velocity profiles along the axial
 183 direction for the (18,0) and (26,0) CNTs are shown in Figure 4. For both cases, the water
 184 flow displays a plug-like velocity profile with mean velocity of *ca.* 3 m/s. It is interesting to
 185 note that the exhibited independence of flow velocity on CNT diameter indicates that the
 186 proposed pump configuration (Figure 1b) may be, in principle, scalable to larger diameters.
 187 However, further investigation is required to confirm this hypothesis.

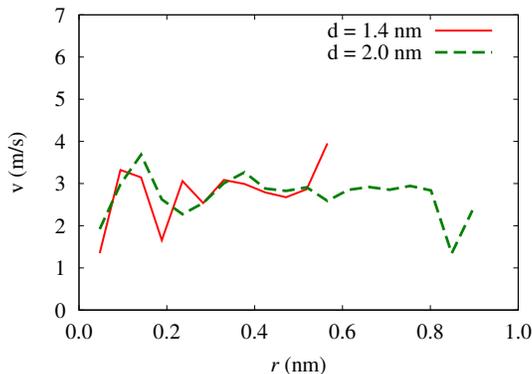


Figure 4: Radial distribution of axial velocity of water inside CNTs of 1.4 nm and 2.0 nm in diameter. The chiralities are (18,0) and (26,0), respectively. The applied thermal gradient is 3 K/nm in both cases.

188 We believe that the present results provide valuable insight in the field of nanofluidic
 189 devices and also open the door to potential practical exploitation of thermal gradients for
 190 driving flow in nanoconduits. It should be noted that large thermal gradients are used in
 191 this study in order to increase the signal-to-noise ratio in our simulations, allowing us to ex-
 192 tract measurable flow data without requiring prohibitively-long simulation times. In fact, for
 193 practical applications in nanofluidic devices wherein the typical distances are in the order of
 194 hundreds of nanometers, the relatively high temperature differences required to impose such
 195 large gradients in the CNT conduits, could give rise to some concern about the boiling tem-
 196 perature of water. Nevertheless, recent studies have reported that water phase transitions
 197 under nanoconfinement may deviate from classical behavior.^{34,35} Specifically, the tempera-
 198 ture for liquid-vapor transition of water confined in CNTs with similar diameters used in
 199 the present study is substantially raised above 100 °C due to nanoconfinement. Therefore,

200 we infer that if a net water flow can be produced imposing a gradient of 0.5 K/nm (see Sup-
201 porting information Figure S15) and assuming the boiling temperature is significantly higher
202 inside the CNT then, the system proposed here could pump liquid water through CNTs with
203 lengths of *ca.* 500 nm. Moreover, nanofabrication techniques currently allow the fabrication
204 of ultrathin membranes connecting two reservoirs separated only by 100 nm.³⁶ This type of
205 ultrathin membranes can be used in combination with vertically-oriented CNTs³⁷ for molec-
206 ular sieving applications or for separation of analytes immersed in water solutions, wherein
207 the flow is driven by thermal gradients, as in the present work.

208 **Conclusion**

209 Using MD simulations, we have investigated the capability of CNTs subjected to a thermal
210 gradient, to sustain continuous and fast water transport in their interior. This study provides
211 the basis for developing a thermal pump based on single-wall carbon nanotubes. The device
212 is able to pump continuous flows with average velocity up to 5 m/s. The mechanisms driving
213 the fluid flow are thermally-induced asymmetric oscillations along the CNT, which propel
214 the fluid in a constant, whip-like motion. Flow rate control is achieved by the direction
215 and magnitude of the imposed temperature gradient and by modifying the position of the
216 pivotal fixed point along the CNT. The interplay between relative positions of the fixed points
217 and the applied thermal gradient produce greater amplitudes in the high-temperature zone
218 compared to the low-temperature zone for specific vibrational modes. We envision that
219 CNTs with thermal gradients could assist the design of nano-chips that require fast water
220 transport between their components.

221 **Methods**

222 To study the rectified flow of water driven by thermal gradients inside the CNT, we perform
223 a series of all-atom MD simulations. The simulations are performed using the MD package

224 FASTTUBE.³⁸ The equations of motion are integrated in time using the leapfrog scheme
225 with a time step of 2 fs. All simulations are conducted in an orthorhombic box with periodic
226 boundary conditions in the axial direction of the CNT and free space conditions in the radial
227 direction. The carbon-carbon intramolecular interactions of the CNT are described by a
228 Morse bond, a harmonic cosine of the bending angle, and a torsion potential.^{16,38,39} Water
229 is modeled by the rigid SPC/E model⁴⁰ and the water-CNT interactions are described by a
230 12-6 LJ potential calibrated for a 81° contact angle.^{16,41} The van der Waals and Coulomb
231 interactions are truncated at 1 nm, while the Coulomb potential is smoothed to ensure energy
232 conservation.^{16,38} The MD package and the force fields have been extensively validated in
233 previous works.^{15–17,38,39,41,42} For details of the potentials, we refer the reader to Zambrano
234 *et al.*¹⁶

235 We first equilibrate the system at 300 K in the NVT ensemble for 0.5 ns. Then, using
236 nonequilibrium molecular dynamics (NEMD) simulations, we impose a thermal gradient
237 along the CNT axis. The thermal gradient is imposed by applying two different tempera-
238 tures at the respective ends of the CNT, as depicted in Figure 1. Specifically, the carbon
239 atoms in each heated zone are coupled to Berendsen thermostats.⁴³ It is important to note
240 that the water molecules are not connected to the thermostat in the NEMD simulations.
241 Previous studies have demonstrated that the Berendsen thermostat is suitable to impose
242 proper nonequilibrium conditions,^{44,45} and is optimal for mechanical responses at relatively
243 constant temperature during CNT compression.⁴⁶ In order to remove spurious effects of the
244 thermostat, the mean velocity of the heated carbon atoms is subtracted, and subsequently
245 added, when the thermostat is applied. We conduct the NEMD simulations during 100 ns to
246 reduce thermal noise, and ensure a steady water flow rate. From the atomic trajectories, the
247 CNT vibrations are analyzed by a FFT algorithm, measuring the amplitudes and frequencies
248 of the different vibrational modes. This FFT method was previously proposed by Pine *et*
249 *al.*⁴⁷ Further details on the simulations and FFT analysis are presented in the Supporting
250 Information.

251 **Acknowledgement**

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255 ceived computational support from the Department of Physics at the Technical University
256 of Denmark.

257 **Supporting Information Available**

258 Simulation protocol, summary of all simulated cases, temperature profile, vibrational (FFT)
259 analysis, water flow vs CNT length, efficiency computation, simulations without fixing points
260 and water flow as a function of the central fixed point position.

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372 **Graphical TOC Entry**

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