Flow of suspensions of carbon nanotubes carrying phase change materials through microchannels and heat transfer enhancement

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This work explores the potential of nano-encapsulated phase change materials (PCMs) in applications related to microelectronics cooling. PCMs (wax or meso-erythritol) were encapsulated in carbon nanotubes (CNTs) by a method of self-sustained diffusion at room temperature and pressure. These nano-encapsulated wax nanoparticles alone allowed heat removal over a relatively wide range of temperatures (different waxes have melting temperatures in the range 40–80 °C). On the other hand, nano-encapsulated meso-erythritol nanoparticles allowed heat removal in the range 118–120 °C. The combination of these two PCMs (wax and meso-erythritol) could extend the temperature range to 40–120 °C, when both types of nanoparticles (wax and meso-erythritol intercalated) would be suspended in the same carrier fluid (an oil). The nanoparticles possess a short response time of the order of 10−7 s. Such nano-encapsulation can also prevent the PCM from sticking to the wall. In this work, experiments with wax-intercalated CNTs, stable aqueous suspensions of CNTs with concentrations up to 3 wt% with and without nano-encapsulated wax were prepared using a surfactant sodium dodecyl benzene sulfonate (NaDDBS). These suspensions were pumped through two channels of 603 μm or 1803 μm in diameter subjected to a constant heat flux at the wall. It was found that the presence of the surfactant in CNT suspensions results in a pseudo-slip at the channel wall which enhances the flow rate at a fixed pressure drop. When aqueous solutions of the surfactant were employed (with no CNTs added), the enhanced convection alone was responsible for a ~2 °C reduction in temperature in comparison with pure water flows. When CNTs with nano-encapsulated wax were added, an additional ~1.90 °C reduction in temperature due to the PCM fusion was observed when using 3 wt% CNT suspensions. In addition, suspensions of meso-erythritol-intercalated CNTs in alpha-olefin oil were used as coolants in flows through the 1803 μm-diameter microchannel. These suspensions (1.5 wt% CNT) revealed a temperature reduction due to the PCM fusion of up to 3.2 °C, and a fusion temperature in the range 118–120 °C.

Introduction

The continuing miniaturization of microelectronic, optoelectronic and radiological devices and powerful computers is accompanied by further increases in their functionality, complexity and integration. According to Moore’s law, the number of chips per circuit is expected to increase exponentially every year, resulting in a dramatic increase in the amount of heat released per unit volume. Thermal reasons have been reported to be responsible for more than half of the failure incidents of microelectronic devices. 1 Therefore effective cooling and temperature reduction become critical issues. Bulky fans and other traditional means have their own severe limitations (e.g. bulky space, thermal inertia, etc.) and can hardly resolve these emerging cooling problems. The use of liquid coolants for cooling microelectronics attracts wider attention. Liquid coolants such as liquid metals 2 and dielectric coolants 3 have been explored in the context of microelectronics cooling. The use of phase change materials (PCMs) holds great promise for the enhancement of cooling. PCMs absorb heat as latent heat of fusion, and release this heat when they solidify elsewhere. 4 Several different types of PCMs are available, such as fatty acids, 5 hydrated salts, paraffin waxes, and eutectic compositions, 6–8 and numerical investigations of potential single-phase or multi-phase PCM effects on microelectronics cooling reveal their benefits. 9–12 Paraffin waxes are attractive PCMs due to their relatively high latent heat of fusion (~200 J g−1), chemical inertness, and minor phase segregation, although their drawbacks are low thermal conductivity and diffusivity. 13 The low thermal conductivity of wax extends its melting time to a level inappropriate for flow-through systems such as microchannels. Efforts to

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enhance the effective thermal conductivity of wax have involved the addition of metallic fillers of a much higher thermal conductivity and diffusivity.\textsuperscript{14-16} The melting time of wax diminishes as a square of the PCM particle size, which has led to the development of nano-encapsulated wax particles inside carbon nanotubes.\textsuperscript{17} In this case the characteristic melting time becomes very short (~10\textsuperscript{-7} s). Nano-encapsulation inside CNTs is also helpful, since it can reduce sticking to the channel walls, and also allows for the operational temperature range to be adjusted by mixing different kinds of waxes with different fusion temperatures.\textsuperscript{17} Potentially the melting temperature band could reach 40–80 °C. Therefore, aqueous suspensions of CNTs with nano-encapsulated waxes hold great potential as effective coolants for microelectronics devices. Similarly to other of methods of microelectronics cooling, heat is removed from the channel section where PCM nanoparticles solidify.

Erythritols are another family of promising organic solid materials which have relatively high latent heats of fusion of the order of 300 J g\textsuperscript{-1}.\textsuperscript{18,19} They are used for the energy storage and could be considered attractive candidates for microelectronics cooling applications.

The present work aims to experimentally investigate heat removal using aqueous suspensions of CNTs with encapsulated wax and with oil-based suspensions of CNTs intercalated with \textit{meso-}erythritol. The coolants flow through straight microcapillaries of circular cross-section embedded in a heated copper block which acts as a prototype of a heated microelectronics device.

### Background formulae

In pressure-driven flows of pure liquids through straight channels of circular cross-section of radius \(a\) with no-slip boundary conditions at the wall, the velocity profile is parabolic\textsuperscript{20}

\[
v = -\frac{1}{4\mu} \frac{dp}{dz} \left(1 - \frac{r^2}{a^2}\right) \tag{1}
\]

and the corresponding volumetric flow rate is given by the Poiseuille law

\[
\dot{Q} = \frac{\pi a^4 dp}{8\mu} \frac{dz}{dz} \tag{2}
\]

In eqn (1) and (2) \(v\) is the longitudinal velocity in the direction of the channel axis \(Oz\), \(\dot{Q}\) is the volumetric flow rate, \(\mu\) is the fluid viscosity, and \(dp/dz < 0\) is a constant pressure drop. Eqn (1) and (2) imply fully developed laminar flows.\textsuperscript{20,21}

In the case of a given constant heat flux at the channel wall, the temperature profile is given by\textsuperscript{22}

\[
T - T_e = \frac{1}{\alpha} \frac{dT_e}{dz} \left[\frac{r}{a} \frac{\alpha}{r} \frac{\alpha}{a} \right. - \frac{1}{4} \left(\frac{r}{a}\right)^2 \right] \tag{3}
\]

where \(\alpha\) is the fluid thermal diffusivity, \(v_c\) and \(T_e\) are the axial velocity and temperature at the channel axis, and \(dT_e/dz\) is the temperature gradient along the channel which is a given constant. Eqn (3) implies laminar flow which is fully developed hydro-dynamically and thermally.

To evaluate the expected temperature reduction \(\Delta T\) due to the presence of PCM-containing CNTs, the following thermal balance is used

\[
\rho c_p \dot{V} \Delta T = L \rho \phi \nabla \tag{4}
\]

where \(\rho\) and \(c_p\) are the fluid density and specific heat, respectively, \(V\) is the total volume of the suspension, \(\phi\) is the PCM volume fraction, and \(L\) is the latent heat of fusion. Then,

\[
\Delta T = \frac{L}{c_p} \frac{\dot{V}}{\rho \phi} \tag{5}
\]

It is emphasized that the PCM volume fraction \(\phi\) can be affected by flow. In particular, CNT alignment by flow in microchannels can effectively increase the local value of \(\phi\) compared to that in the solution bulk, and thus enhance the temperature reduction \(\Delta T\), as the experimental results discussed below reveal.

Note also, that the present work is aimed at the cooling of microelectronic devices with PCM suspensions. That determines our usage of eqn (1)- (3) valid for laminar flows in microchannels relevant in the present case.

### Experimental

#### Materials

In the experiments with wax-intercalated CNTs, carbon nanotubes PR24XT-LHT-AM of small aspect ratio \(\kappa \sim 142\) were acquired from Pyrograf Products. Surfactant NaDDBS (sodium dodecyl benzene sulfonate) was supplied by Sigma-Aldrich. Mustard oil of viscosity 76.5 cP was purchased in a grocery store. Carbon nanotube suspensions were prepared as follows: 1.5 g of a previously prepared 1 wt% aqueous solution of NaDDBS was mixed with 18.5 g of 0.1 wt% aqueous suspension of empty CNTs. Similarly, 2 wt% suspension of NaDDBS was added to 0.2 wt% CNT suspension, etc. for the other wt% values for the empty CNT suspensions. The mixtures were sonicated in a 55 W ultrasonic bath sonicator. Benzene and wax\textsuperscript{17} (melting point in the range 45–47 °C) were obtained from Sigma-Aldrich.

For the preparation of wax-intercalated CNT suspensions, the method of self-sustained diffusion\textsuperscript{17,23,24} was used. First, wax solution in benzene was prepared by dissolving 0.3 g of wax in 19.7 g of benzene. The solution was sonicated for 30 min. After that, 60 mg of empty CNTs were added to the wax solution and sonicated for 2–3 min. The CNT suspension in wax solution was then left to evaporate in a chemical hood. As the benzene evaporated, wax diffused into the CNTs. Since the wax concentration in the solution was permanently increasing during evaporation, the concentration gradient was self-sustained and wax continued to diffuse...
into CNTs which were significantly intercalated with wax. After the evaporation was finished, the dry CNTs intercalated with wax were rinsed in benzene to remove any wax deposited outside and sonicated for a further 2 min. The suspensions of CNTs in benzene were filtered and the resulting wax-intercalated CNTs were used to prepare the suspension in water.

To prepare aqueous suspensions of wax-intercalated CNTs, a probe sonicator of 500 W [20 kHz (Qsonica)] was employed along with the bath sonicator. Prior to using the bath sonicator, the probe sonicator was used for 5 min at 40% power. That helped to remove the residual chunks as wax can increase the tendency of CNT clustering. The pre-sonication with the probe sonicator allowed a reduction in the duration of bath sonication to 5 h. The 1 g surfactant solution was handled similarly to the above-mentioned 19 g suspension. Namely, 0.5 g of surfactant solution was added prior to probe sonication, the rest of surfactant solution was added during the bath sonication in steps. Namely, 0.1 g of surfactant solution was added to the suspension after every hour of sonication.

In the experiments with the meso-erythritol-intercalated CNTs, the same carbon nanotubes PR24XT-LHT-AM of small aspect ratio $\kappa \sim 142$ were used. Meso-erythritol (melting point in the range 118–120 °C) was obtained from Sigma-Aldrich. The method of self-sustained diffusion was applied again to prepare CNTs intercalated with meso-erythritol. Specifically, 3 g of erythritol was dissolved in 27 g of water, and the solution was sonicated in the bath sonicator for 30 min until it became homogeneous. After that, 0.3 g of empty CNTs were added to the solution and sonicated for an additional 2–3 min. The mixture was left in the chemical hood until the complete evaporation of water. As water evaporated from the solution, erythritol diffused into the CNTs. It is emphasized that the erythritol concentration in the solution was inevitably increasing during evaporation of water, which sustained the erythritol concentration gradient towards the nanotubes in the mixture. As a result, erythritol continued to diffuse into the empty CNTs during the entire evaporation process and they were quite significantly intercalated with the PCM. After the evaporation finished, the dry intercalated CNTs were rinsed with water under sonication for 1 min to remove any additional erythritol from the outside surfaces. After that, the CNTs were removed by filtration and the resulting CNTs intercalated with erythritol were used to prepare the suspension in oil as described below.

The suspending medium was low viscosity alpha-olefin oil, which was provided by Chevron Phillips Chemical Company. According to the manufacturer’s specification, the kinematic viscosity of the oil at 40 °C is 5.2 cSt and density is 6.646 lb gal$^{-1}$ (0.663 g cm$^{-3}$). The same surfactant, as for the aqueous wax-CNT suspensions, sodium dodecyl benzene sulfonate (NaDDBS) was also used in the present case. The heat removal experiments were conducted using a 1.5 wt% CNT suspension. The suspension was prepared as follows: 2 g of a previously prepared 10 wt% solution of surfactant (NaDDBS) in oil was mixed with 18 g of 1.5 wt% CNT suspension in the same oil. The mixture was initially sonicated using a 500 W probe sonicator [20 kHz (Qsonica)] for 5 min at 40% power. It was then sonicated in the 55W bath sonicator for 6 hours.

**Experimental setup**

In the setup used to study pure water or aqueous surfactant solutions flows, two 10 ml syringes were coupled and glued with epoxy to make an oil chamber (Fig. 1). For each new experimental run, the mustard oil in the chamber was changed. The experimental setup shown in Fig. 1 also incorporates an air-driven piston which pushes oil inside the oil chamber. The oil, in turn, pushes pure water or aqueous solutions of surfactants into the chamber was found to be unstable.

The microchannel used in the setup shown in Fig. 1 was a 25G stainless steel needle with an ID of 260 μm. The air pressure was monitored from the primary air-line, and the pressure maintained at the top of the oil chamber could be measured with the help of the pressure gauge. Two DSLR cameras were employed to capture images. One of the cameras recorded the pressure and time readings, while the other one recorded the volume change in the water/suspension chamber. The imaging was done simultaneously using a wired trigger, every 30 s. The recorded time, pressure and volume were used to evaluate the corresponding flow rate. The data were averaged over two consecutive trials.

In the experiments on cooling using aqueous suspensions of CNTs intercalated with wax, a peristaltic pump was included in the system instead of the air pressure driven system to sustain the flow for a long time (Fig. 2). The peristaltic pump was purchased from New Era Pump Systems Inc. In this case 20G or 13G needles (603 and 1803 μm ID, respectively) were used as microchannels. The aqueous suspensions of CNTs intercalated with wax or the oil-based suspensions of CNTs intercalated with erythritol were re-circulated through the microchannels by means of the peristaltic pump. The suspensions were pumped from the
reservoir at a specific flow rate through the microchannel embedded in the heated copper block. The returning suspension was then passed through a cooling section which was kept at 12 °C by cooling water re-circulating around the microchannel (see Fig. 2). The experiments with the aqueous suspensions of CNTs intercalated with wax were conducted at different flow rates ranging from 5 ml min\(^{-1}\) to 55 ml min\(^{-1}\) preset at the pump. The experiments with the oil-based suspensions of CNTs intercalated with erythritol were conducted at flow rates ranging from 25 ml min\(^{-1}\) to 65 ml min\(^{-1}\).

Two 50 W heaters received from Omega were used to heat the copper block of lateral dimensions 1.5 cm × 1.5 cm and length 3.175 cm which was a prototype of a heated integrated microelectronic system. Heating was sustained at a constant level of 9 W for the aqueous suspensions of wax-intercalated CNTs and 20 W for the oil suspensions of erythritol-intercalated CNTs maintained with the help of a transformer. The microchannel was placed inside the copper block and properly tightened with screws. Silver paste was used in the gap between the microchannel and copper block to ensure proper contact and guarantee unperturbed heat transfer from the block to the suspension. Two thermocouples purchased from Omega were used to measure the temperature distribution along the heating section. The thermocouples were embedded in the copper block microchannel assembly (Fig. 2). One thermocouple was embedded at the very entrance of the needle to measure the inlet temperature, and the other one was embedded in the middle of the copper block to measure the microchannel temperature there. The latter was considered as the average temperature of the channel. All temperature measurements were done using an Omega H8065W thermometer. The experiments with aqueous suspensions of the wax-intercalated CNTs were usually conducted with an initial copper block temperature of 60 °C. On the other hand, the experiments with oil-based suspensions of the erythritol-intercalated CNTs were conducted with an initial copper block temperature of 145 °C. Note that for the latter suspensions, the setup in Fig. 2 was used to study the cooling effect of the oil itself, of the oil-surfactant mixture, of the empty CNT suspension, and the suspension of erythritol-intercalated CNTs.

Results and discussion

Water and aqueous solution of surfactant flows through microchannels

In the experiments pressure drop was the governing parameter, while volumetric flow rate was measured. The experimental results for pure water flows are plotted in Fig. 3 together with the Poiseuille law given by eqn (2). Fig. 3 shows that the agreement between the theoretical and experimental results is very good, which verifies the accuracy of the measurements. It is emphasized that the extra pressure drop between the pressure gauge and the microchannel entrance is practically negligible. So, it can be safely assumed that the pressure at the microchannel entrance is the same as that on the pressure gauge.

The flow is definitely laminar since the Reynolds number Re = 9.774 at the flow rate which corresponds to the pressure drop of 6 psi. The Reynolds number Re = \( \frac{\rho VD}{\mu} \) where \( \rho \) is the fluid density, \( V \) is the average velocity and \( D \) is the channel cross-sectional diameter.

The entrance length \( \ell_e \) at which a fully developed flow in a microchannel will be formed is found using

\[
\ell_e = \frac{0.6}{1 + 0.035Re} + 0.56Re
\]

In the present case \( \ell_e = 0.15 \text{ cm} \) which is much less than the microchannel length \( \ell = 5 \text{ cm} \). Therefore, there is practically a fully developed flow from the very beginning of all microchannels used in the present work.

The CNT suspensions were stabilized with different surfactants, which were beneficial in that these reduced the tendency of microchannel clogging. The CNTs are apparently hydrophobic which does not allow them to disperse in water properly. This can enhance the viscous losses during pumping the suspension even when a moderate concentration of CNTs is used. The apparent hydrophobicity of the CNTs in polar solvents such as water stems from the fact that they have sufficiently high aspect ratios and flexibilities.
Therefore, a strong van der Waals attraction between them results in the formation of a tightly entangled (rope-like) structure with dense packing.\textsuperscript{26} Dispersion of CNTs can be facilitated by ultra-sonication or shear mixing, by means of functionalization with acids, or by using surfactants to modify surface characteristics in favor of tube hydration and prevention from agglomeration. However, ultra-sonication or shear mixing, as well as the acid treatment often lead to surface fracture.\textsuperscript{26} Surfactants are a better way to disperse CNTs in water. There have been reports on the application of different surfactants, e.g. sodium dodecyl sulphate (SDS) or sodium dodecyl benzene sulfonate (NaDDBS) which are claimed to be better than some organic surfactants.\textsuperscript{27,28} NaDDBS is superior, since it has a benzene ring attached to it, which is adsorbed onto the CNTs with the help of $\pi$-interactions.\textsuperscript{26} Sonication allows the entangled CNT bundles to disperse and thereby enhances the surfactant molecules adsorption on individual CNTs.\textsuperscript{29} With NaDDBS added, it was found that the maximum concentration of CNTs at which clogging does not occur in the 260 $\mu$m microchannel is 1 wt%. Beyond that limit, CNT aggregates clog the entrance of the microchannel. Volumetric flow rates of CNT suspensions with added surfactant were measured at different pressure drops and the results are shown in Fig. 4.

Fig. 4 shows that the CNT suspensions with the added surfactant demonstrate much larger volumetric flow rates than the pure solvent at the same pressure drop (the flows of the pure solvent correspond to the Poiseuille law), even though the presence of particles should increase the effective viscosity. The reason for the observed flow enhancement might be associated with the presence of the surfactant. To verify this hypothesis, experiments were conducted with the aqueous 0.5 wt% solution of surfactant without CNTs. The results are shown in Fig. 5. The flow rate of the surfactant solution was significantly higher than that of pure water at the same pressure drop, which confirms that the observed flow enhancement is due to the surfactant. Note, that the shear viscosity of the surfactant solution, measured using an LV-II$+$ cone and plate Brookfield viscometer was found to be 1 cP, which is the same as that of water. Surfactant molecules can be tethered at the microchannel and effectively displace water from the wall, resulting in a pseudo-slip. The surfactant “forest” at the wall can also trigger degassing and formation of nanobubbles near the wall which also facilitate slip.\textsuperscript{30–32} To diminish the presence of the entrapped gas in solutions, these were left for 30 min after sonication to let bigger bubbles be removed by buoyancy. As pressure drops down in the flow along the microchannel, degassing (according to Henry’s law) can also result in the formation of nanobubbles. The latter is corroborated by the fact that the flow enhancement at higher pressure drops was more significant than at the lower ones (cf. Fig. 4 and 5).

It should be emphasized that bubbles anchored on the tethered surfactant molecules at the microchannel wall do not necessarily form a continuous gas layer near the wall, and are still capable of providing a significant slip.\textsuperscript{32} Since the bubble layer near the wall is discontinuous and does not form an insulation layer, no temperature jump is expected at the wall.

According to ref. 33, volumetric flow rate increases due to a slip at the microchannel wall according to the following expression

\[
\frac{Q_s}{Q_{NS}} = 1 + 4 \frac{\lambda}{a}
\]

where $Q_s$ is the flow rate with a slip, $Q_{NS}$ is the flow rate without slip which is given by eqn (2), and $\lambda$ is the slip length.

The data in Fig. 4 were used to determine the effective slip lengths corresponding to the flows of CNT suspensions with surfactant. The results are shown in Fig. 6. The slip length of the order of tens of microns is a clear manifestation of liquid displacement from the wall, in particular due to the formation of gas pockets triggered by tethered surfactant molecules. The slip length increases with CNT concentration, since the surfactant presence increases proportionally. As a result, a denser “forest” of surfactant molecules is tethered at the wall with more entrapped gas, and water displacement from the wall becomes more severe.
Intercalation of wax in CNTs

As the next step, CNT suspensions intercalated with wax were prepared. Wax intercalation into CNTs was conducted using 0.5 wt% NaDDBS surfactant solution. The experimental data are shown by symbols. The straight line shows the predictions using the Poiseuille law, eqn (2).

**Fig. 4** Volumetric flow rate of CNT suspensions versus pressure drop at the following CNT concentrations: (a) 0.1 wt%, (b) 0.2 wt%, (c) 0.6 wt%, (d) 0.9 wt%, and (e) 1 wt%. The experimental data are shown by symbols. Straight lines show the predictions using the Poiseuille law, eqn (2).

**Fig. 5** Enhanced flow rate in 0.5 wt% NaDDBS surfactant solution. The experimental data are shown by symbols. The straight line shows the predictions using the Poiseuille law, eqn (2).

**Fig. 6** The average slip length versus CNT concentration.

Intercalation of wax in CNTs

As the next step, CNT suspensions intercalated with wax were prepared. Wax intercalation into CNTs was conducted using...
the method of self-sustained diffusion as described in ref. 17. The observations of the wax-intercalated CNTs were performed using a JEOL JEM 3010 Transmission Electron Microscope (TEM). The images shown in Fig. 7 clearly reveal the presence of wax in the CNT bore with no wax deposits on the outside walls.

In addition to the TEM observations, DSC measurements were also conducted to quantify the amount of the intercalated wax. For that, 2.07 mg of a wax-intercalated CNT sample (see Fig. 7) was heated at 5 °C min⁻¹ in a N₂ atmosphere up to 75 °C. A representative thermogram is shown in Fig. 8. According to the manufacturer’s specification, the CNTs used in this work have an ID ~35 nm, an OD ~55–90 nm and a length ~10–30 μm. These data were used to evaluate the amount of wax encapsulated in the sample and responsible for its heat removal due to the heat of fusion. The heat absorbed during DSC measurement due to wax melting (corresponding to the endothermic peak in Fig. 8) was 51.75 mJ for 2.07 mg sample mass. Using the CNT volume, the wax density of 0.9 g cm⁻³ and the CNT density of 1.6 g cm⁻³, the mass fraction \( m_w \) of wax in the sample is found to be 0.1378. Then, the total mass of wax in the sample was 0.327 mg. The total heat of fusion of wax is then \( H = m_w L \), which has a measured value of 51.75 mJ. Correspondingly, the specific heat of fusion \( L \) is equal to 158 J g⁻¹. This result is commensurate with the value of 141 J g⁻¹ reported for bulk samples of the same wax (melting point 45–47 °C). The small difference in the values of \( L \) stems from the fact that the mass of wax intercalated in CNTs has been calculated here using the average aspect ratio and the inner diameter of CNTs. Our result for \( L \) shows that the CNTs were completely intercalated with wax with no deposits on the outside walls. This corroborates the direct observations in Fig. 7.

**Intercalation of erythritol in CNTs**

The intercalation of erythritol into CNTs was conducted using the method of self-sustained diffusion. The observations of the erythritol-intercalated CNTs were carried out using a JEOL JEM 3010 Transmission Electron Microscope (TEM). The images shown in Fig. 9 reveal the presence of erythritol encapsulated in the CNT bore with practically no PCM deposits on the outside walls.

**Flow rates of aqueous suspensions of wax-intercalated CNTs**

Flow rates of different aqueous suspensions of CNTs intercalated with wax measured at different pressure drops are depicted in Fig. 10. Similarly to the results for aqueous suspensions of empty CNTs in Fig. 4, the results in Fig. 10 demonstrate a higher flow rate of suspensions than that of pure water at the same pressure drop. As before, this effect is attributed to the presence of surfactant. As distinct from the empty CNTs, clogging takes place at a lower CNT concentration, namely suspensions of 1 wt% were clogging the microchannel with CNTs intercalated with wax but not with the empty CNTs in Fig. 4 (where a 260 μm channel was used).

**Heat removal with aqueous wax-intercalated CNT suspension flows**

Four different types of coolants were used for comparison in the heat removal experiments in the present sub-section: pure water, aqueous solutions of surfactant NaDDBS, an aqueous suspension of the empty CNTs, and an aqueous suspension of the wax-intercalated CNTs. All measurements were started from an average temperature of the copper block of 60 °C at a constant heat flux of heating of 9 W. Fig. 11–13 show all the recorded temperature histories of the copper block as coolants were flowing through the microchannel embedded in it. Fig. 11 shows the plots of the temperature/time dependence in the case of 1 wt% suspensions flowing through a...
603 μm channel. Fig. 12 and 13 were plotted for 2 wt% and 3 wt% suspensions flowing through the 1803 μm channel, respectively. The panels on the right hand side in Fig. 11 show that in the range of flow rates from 5 to 35 ml min\(^{-1}\), the most effective cooling (and thus, the lowest steady-state temperature \(T_s\)) is achieved by the aqueous suspension of wax-intercalated CNTs. At flow rates higher than this range, the residence time of coolant material elements in the microchannel becomes too small (of the order of 1 s), the solvent carrying CNTs does not reach a high enough temperature, and thus, the wax intercalated in the CNTs does not undergo melting and removes no latent heat of fusion. The characteristic thermal transient time in the present case would be of the order of 1 s. Fig. 11 shows the lowest values of the temperature plateaus in the case of the CNT suspension compared to that of pure water at the flow rates of 5 and 25 ml min\(^{-1}\). This might imply that the temperature reduction is caused by the presence of the surfactant. However, to prepare a stable suspension of CNTs, the surfactant was added. It was shown above that the surfactant presence results in nano-scale bubbles which cause slip in the shear flow near the channel wall \(\text{cf.} \) Fig. 5). That enhances the flow rate in the channel. To verify this, a similar series of tests were conducted with an aqueous solution of the surfactant prepared similarly to the CNT suspension. These tests were conducted at the same flow rates as those using the CNT suspensions. The results of these tests revealed a similar temperature reduction for the same range of flow rates \(\text{cf.} \) Fig. 11). This clearly indicates that the temperature reduction stems not only from the presence of the CNTs but partially originates from the higher flow rates due to the presence of the surfactant, which facilitates the enhanced convective heat transfer.

Fig. 11 shows that the steady-state temperatures achieved with the aqueous suspensions of the wax-intercalated CNTs are 0.6–1.3 °C lower than those with the aqueous suspensions of the empty CNTs, whereas the later reduced the temperature by 1 °C compared to pure water at the lowest and moderate flow rates of 5 and 25 ml min\(^{-1}\) due to the presence of surfactant. At 5 ml min\(^{-1}\) the maximum effect of the temperature drop (1.3 °C) due solely to the PCM melting was observed, whereas at 25 ml min\(^{-1}\) an optimum combination of both convective heat removal and PCM fusion was recorded.

In addition, careful examination of Fig. 11 shows that at the higher flow rate (55 ml min\(^{-1}\)) the temperature reduction in water flow is larger than that in the CNT suspension flows at these flow rates. The probable reasons are the following. (i) At the high flow rates the CNT residence time in the hot section is too short for wax melting, so no latent heat of wax fusion is involved, while the heat capacity of the CNTs is less than that of water they replaced. (ii) At the higher flow rates more bubbles are shed from the wall covered by surfactant layer and tethered on the CNTs which also prevents wax melting.
The experiments conducted with the higher concentrations (2 wt% and 3 wt%) of the wax-intercalated CNT suspensions flowing through the 1803 μm microchannel showed (cf. Fig. 12 and 13) a larger cooling effect compared to that of the 1 wt% suspension in Fig. 11. In the case of the 2 wt% wax-intercalated CNT suspension, a maximum temperature
Fig. 12  Temperature of the copper block versus time in the case of flows of water, surfactant solution, 2 wt% suspension of the empty CNTs, and 2 wt% of wax-intercalated CNTs in 1803 μm channel. The panels show the temperature histories corresponding to the following rates of the coolant flow: (a1) and (a2) correspond to the flow rate of 5 ml min\(^{-1}\), (b1) and (b2) to 25 ml min\(^{-1}\), (c1) and (c2) to 45 ml min\(^{-1}\), (d1) and (d2) to 55 ml min\(^{-1}\). The panels marked with numeral 1 reveal the transient phase, whereas those marked with numeral 2 show the subsequent steady-state stage. Black symbols correspond to pure water, red symbols to the aqueous surfactant solution, green symbols to the aqueous suspension of the empty CNTs, and blue symbols to the aqueous solution of the wax-intercalated CNTs. The values of the steady-state temperature \(T_s\) reached are shown by the corresponding colors. For the experiments at a flow rate of 5 ml min\(^{-1}\) the inlet coolant temperature was 23.6°C, whereas for the other experiments it was 20.2°C. The rectangular domains in the left hand side panels corresponding to the steady-state regimes are shown in detail in the right hand side panels.
Fig. 13  Temperature of the copper block versus time in the case of flows of water, surfactant solution, 3 wt% suspension of the empty CNTs, and 3 wt% of wax-intercalated CNTs in 1803 μm channel. The panels show the temperature histories corresponding to the following rates of the coolant flow: (a1) and (a2) correspond to flow rates of 5 ml min⁻¹, (b1) and (b2) to 25 ml min⁻¹, (c1) and (c2) to 45 ml min⁻¹, (d1) and (d2) to 55 ml min⁻¹. The panels marked with numeral 1 correspond to the transient phase, whereas those marked with numeral 2 to the subsequent steady-state stage. Black symbols correspond to pure water, red symbols to the aqueous surfactant solution, green symbols to the aqueous suspension of the empty CNTs, and blue symbols to the aqueous solution of wax-intercalated CNTs. The values of the steady-state temperature $T_s$ reached are shown by the corresponding colors. For the experiments at the flow rate of the 5 ml min⁻¹ the inlet coolant temperature was 23.6 °C, whereas for the other experiments it was 20.2 °C. The rectangular domains in the left hand side panels corresponding to the steady-state regimes are shown in detail in the right hand side panels.
reduction of 2.2 °C was found due to the wax fusion at 5 ml min⁻¹ flow rate (compare with 1.3 °C in Fig. 11). At this low flow rate the low flow velocity of 1 cm s⁻¹ results in a longer residence time of the PCM-intercalated CNTs in the channel (~3 s). This is longer than the characteristic thermal transient time in the channel which is of the order of 1 s, and definitely much longer than the characteristic time scale for wax melting inside a CNT which is of the order of ~10⁻² s. Note that a lower flow rate also diminishes the convective cooling component. It should be also emphasized that even for the 2 wt% wax-intercalated CNT suspension the viscous dissipation was still negligibly small, since the measured shear viscosity was very close to that of water, namely 1.08 cP.

The maximum effect of the 2 wt% wax-intercalated CNT suspension in cooling was found at 25 ml min⁻¹ where the total wall temperature reduction was 3.4 °C, of which 1.4 °C was due to the wax melting (Fig. 12). At the flow rate of 45 ml min⁻¹ a considerable temperature reduction was still visible with the 2 wt% wax-intercalated CNT suspension, since in the bigger channel the flow velocity was smaller and the residence time longer as compared to the smaller channel in Fig. 11. Only at the flow rate of 55 ml min⁻¹ the effect of cooling due to the wax fusion was diminished to the level of the 1 wt% wax-intercalated CNT suspension in the smaller channel.

The experiments with the 3 wt% wax-intercalated CNT suspension were conducted next. The results are plotted in Fig. 13. These show that at the lower flow rate of 5 ml min⁻¹ a significant temperature reduction due to wax melting was observed (up to 3.9 °C reduction). At the intermediate flow rate of 25 ml min⁻¹, the suspension was not better than the surfactant solution as a coolant. Two probable reasons of this phenomenon could be mentioned. First, a lower specific heat material (wax in the CNT and the CNTs themselves) replaced a higher specific heat material (water). Second, the presence of a significant amount of CNTs increases the effective viscosity of suspension, which reduces the flow rate at a given pressure drop, and thus diminishes convective heat transfer. The measured shear viscosity of the 3 wt% CNT suspension was 1.38 cP compared to 1 cP of water, which enhances the viscous losses and diminishes cooling. The cooling effect (both, due to the wax melting in the CNTs and the convective component) was enhanced at the flow rates of 45 ml min⁻¹. At 55 ml min⁻¹ PCM fusion was responsible for a 2 °C reduction in the steady-state temperature compared to the corresponding case of suspension of the empty CNTs.

These experiments with the 3 wt% suspension of the wax-intercalated CNTs were repeated at all flow rates for longer times. The repeatability of the results was fully verified with the error bars being negligibly small. The repeatability of the results irrespective the experiment duration also sheds light onto the origin of air bubbles resulting in the observed slip. One could assume the following two possibilities for the air bubbles to emerge. (i) When a suspension enters a dry microchannel, air can be entrapped in the emerging forest of the tethered surfactant molecules at the microchannel wall. (ii) The dissolved air is being released from the suspension according to Henry’s law (since it flows toward the lower pressure end), the bubbles migrate to the wall and are anchored there. If mechanism (i) would be important, then the slip effect would be transient, and disappear in long experiments over time, because the trapped air would be washed away or dissolved. On the other hand, if mechanism (ii) is relevant, there should be no fading of the slip effect. The latter, in fact, happens, which confirms that the anchored bubbles responsible for the slip are sustained due to Henry’s law. Since liquids inevitably contain some air, either due to diffusion from the surrounding atmosphere, or a prior processing, pressurization followed by de-pressurization in microchannel flows inevitably leads to bubble formation due to Henry’s law and a sustainable slip effect.

The value of ΔT predicted by eqn (5) using the parameters $L = 158 \text{ J g}^{-1}$, $\eta_{p,\text{suspension}} = 4.08 \text{ J (g x K)}^{-1}$, and the volume fraction $\phi = 5.26 \times 10^{-3}$ is 0.204 °C for 3 wt% suspension. The specific heat of suspension was calculated using the following expression:

$$c_{p,\text{suspension}} = (c_{p,\text{water}} + \phi) \times c_{p,\text{CNT}}/\phi,$$

where $c_{p,\text{water}} = 4.18 \text{ J (g x K)}^{-1}$ and $c_{p,\text{water}} = 2.2 \text{ J (g x K)}^{-1}$, $c_{p,\text{CNT}} = c_{p,\text{carbon}} = 0.71 \text{ J (g x K)}^{-1}$ and $c_{p,\text{water}} = 1.9 \text{ J (g x K)}^{-1}$. The masses of water, wax and CNTs were calculated as discussed previously. The calculated value of ΔT is significantly lower than the maximum temperature reduction of 1.9 °C measured in the experiments. It means that the CNT alignment by flow in microchannels can effectively increase the local value of $\phi$ compared to that in the solution bulk, and thus enhance the temperature reduction ΔT.

It is worth mentioning that it was impossible to work with more concentrated suspensions of CNTs (with concentrations above 3 wt%). This is related to the high aspect ratio of CNTs. The aspect ratio of carbon nanotubes plays a very important role beginning from the suspension preparation. For a fixed weight percentage the aspect ratio of CNTs determines whether a suspension is dilute or semi-dilute, and thus the flow regimes. In particular, in semi-dilute suspensions hydrodynamic particle–particle interactions can become so significant that a microchannel flow cannot be sustained. Suspensions of elongated particles (e.g. CNTs) are dilute if $\phi \ll \kappa^{-2}$, where $\phi$ is the volume fraction and $\kappa$ is the particle aspect ratio. For a 3 wt% CNT suspension $\phi$ is about 0.03 and $\kappa^{-2} = 5 \times 10^{-5}$, i.e. the suspension is already semi-dilute ($\kappa^{-2} < \phi < 1$) and significant hydrodynamic particle/particle interactions are present and increase resistance to flow. In particular, CNTs tend to orient along the channel and form aggregates effectively clogging it.

Note also that the effect of the thermal resistance associated with the nanotube wall can be estimated as follows. Consider, for example, a CNT suspension at a flow rate of 25 ml min⁻¹ (which is 0.42 ml s⁻¹) subjected to 9 W of thermal energy transferred through the microchannel wall (as measured in the present case). In 0.42 ml which passes through the microchannel per second the number of particles is of the order 10¹¹ (estimated using the known CNT content, 2 wt%, and mass of an individual CNT, 8.6 $\times 10^{-14}$ g). Accounting for the heat...
received by wax, we find that each individual nanotube is subjected to $Q = 3.7 \times 10^{-10}$ W. The thermal resistance of a cylindrical cell (CNT) is $R_\text{w} = (2\pi k \ell_{\text{CNT}})^{-1} \ln(r_o/r_i)$ where $r_o$ and $r_i$ are the outer and inner cross-sectional radii, respectively, with $r_o/r_i = 2$, and $k$ being the thermal conductivity of CNTs [10$^3$ W (m x K)$^{-1}$ (as per manufacturer)]. The CNT length is $\ell_{\text{CNT}} \approx 10$ μm. Since the temperature difference at the CNT wall $\Delta T_{\text{w}} = QR_\text{w}$, we find that $\Delta T_{\text{w}} \approx 10^{-9}$ K, which is negligibly small. In addition, the thermal response time of CNT wall of the thickness $h = r_o - r_i$ is of the order of $\tau = h^2/\alpha$ where $\alpha$ is the thermal diffusivity of CNT. This estimate yields $\tau \sim 10^{-11}$ s, which is also negligible. The estimate is obtained under the assumption that in a good suspension stabilized with surfactants, there is no air layer at the outer CNT wall and it is in direct contact with the carrying liquid.

**Heat removal with flows of oil-based erythritol-intercalated CNT suspensions**

In the heat-removal experiments with the oil-based erythritol-intercalated CNT suspensions, four different types of coolants were compared: pure alpha-olefin oil, the solution of surfactant NaDDBS in oil, the oil-based suspension of the empty CNTs, and the oil-based suspension of the erythritol-intercalated CNTs. The need for the oil-based suspensions is due to the fact that the melting point of erythritol is in the range 118–120 °C, above the boiling temperature of water, which excludes the latter as a carrier fluid. All the measurements were started from an average initial block temperature of -145 °C and were conducted at a constant heat flux of 20 W. Fig. 14 shows the recorded temperatures of the copper block as the oil-based coolants were flowing through the microchannel (13 gauge needle, 1803 μm in diameter) embedded in it. Fig. 14 corresponds to the 1.5 wt% suspension flows. All the results on the right-hand side in Fig. 14 show that in lower flow rates range from 25 to 45 ml min$^{-1}$ the most effective cooling, and correspondingly, the lowest steady-state temperature $T_C$ of the copper block was achieved in the experiments with the oil-based suspension of erythritol-intercalated CNTs. At the higher flow rates, i.e., 55 ml min$^{-1}$ and 65 ml min$^{-1}$, the residence time of the coolant material elements in the microchannel is already very small (of the order of 1 s). As a result, the oil-based CNT suspension could not reach the high enough temperature in the channel needed for the erythritol melting. Therefore, the erythritol intercalated in the CNTs could not undergo complete melting and utilize its latent heat of fusion. Fig. 14 also show the lowest values of the temperature plateaus for the oil-based surfactant solution compared to that of the pure oil at almost all flow rates. This might be interpreted as a decrease of viscosity of the surfactant solution compared to the original oil, which would result in an increased flow rate. Measurements of the shear viscosity were conducted for both pure oil and the oil-based surfactant solution at 25 °C using an LV-II+ cone and plate Brookfield viscometer, at a shear rate of 112 s$^{-1}$. For both liquids a viscosity of 6.8 cP was measured disproving the above-mentioned interpretation. However, it was found that when the surfactant was added to oil, it caused production of air bubbles as the solution impinged the reservoir after leaving the channel. Since the oil has a lower surface tension of 31 dyn cm$^{-1}$ than that of water (72 dyne cm$^{-1}$), the bubbles in oil still existed in the re-circulating flow in the channel. These might even be very small nano-sized bubbles. Such nano-sized bubbles could cause pseudo-slip, which can indeed enhance the apparent flow rate and thereby result in an enhanced convective heat transfer compared to the one produced by pure oil. On the other hand, this was not the case with the oil-based CNT suspensions with the surfactant, for which the shear viscosity at room temperature was measured as 9.4 cP, almost 35% higher than that of the surfactant solution.

Fig. 14 shows that the steady-state temperatures achieved with the oil-based suspensions of the erythritol-intercalated CNTs are by 0.5–3.2 °C lower than those achieved with the oil-based suspensions of the empty CNTs. Table 1 shows the measured temperature drop (in comparison to the suspension of the empty CNTs) due to the erythritol melting in CNTs in steady-state regimes for different flow rates. In addition note that the oil-based suspensions of the empty CNTs had practically the same cooling effect as the pure oil due to the balancing the effect of the surfactant induced-slip by the increased viscosity due to the CNT presence. The results in Table 1 show that the longer residence time in the channel maximized the erythritol melting and its cooling effect.

To evaluate the expected temperature drop $\Delta T$ due to melting of the erythritol intercalated in CNTs, eqn (5) is used again. The specific heat capacity value of the suspension in the present case can be evaluated using the following formula $c_p,\text{suspension} = (c_{p,\text{oil}} + \phi c_{p,\text{erythritol}} + M_{\text{CNT}} c_{\text{p,CNT}})/M_{\text{total}}$ where $c_{p,\text{erythritol}} = 1.4 \text{ J (g x K)}^{-1}$ (ref. 34), $c_{p,\text{CNT}} = 0.71 \text{ J (g x K)}^{-1}$, $\phi = 0.27$ (as per the manufacturer’s specification) all the values for the 140–150 °C temperature range. For 20 g of a suspension, 19.7 g is oil, neglecting the presence of surfactant in the 2 g oil-surfactant solution. For the 0.3 g of CNTs with the intercalated erythritol we use the following data: the erythritol density is 1.45 g cm$^{-3}$, the CNT density is 1.6 g cm$^{-3}$ (as per the manufacturer’s specification), the average ID of CNTs is ~35 nm, the average OD is ~55–90 nm, and the length is 10 μm, the erythritol mass is 0.09 g and the CNT mass is 0.21 g. Then, the volume fraction $\phi$ appears to be 2.06 x 10$^{-3}$. Correspondingly, we find $c_{p,\text{suspension}}$ to be 2.604 J (g x K)$^{-1}$. The latent heat of fusion of erythritol is 339.8 J g$^{-1}$ (ref. 19). Using eqn (5), we find the expected temperature drop, $\Delta T$ as 0.27 °C, which is less than the measured value of 0.5–3.2 °C. As in the case of the aqueous suspensions of the wax-intercalated CNTs, it means that the CNT alignment by flow in microchannels can effectively increase the local value of $\phi$ compared to that in the solution bulk, which results in a larger reduction of the copper block temperature $\Delta T$. 


Fig. 14  Temperature of the copper block versus time in the case of flows of oil, oil-based surfactant solution, 1.5 wt% suspension of the empty CNTs, and 1.5 wt% of erythritol-intercalated CNTs in the 1803 μm channel. The panels show the temperature histories corresponding to the following rates of the coolant flow: (a1) and (a2) correspond to flow rates of 25 ml min$^{-1}$, (b1) and (b2) to 45 ml min$^{-1}$, (c1) and (c2) to 55 ml min$^{-1}$, (d1) and (d2) to 65 ml min$^{-1}$. The panels marked with numeral 1 reveal the transient phase, whereas those marked with numeral 2 the subsequent steady-state stage. Black symbols correspond to pure oil, red symbols to the oil-based surfactant solution, green symbols to the oil-based suspension of the empty CNTs, and blue symbols to the oil-based suspension of the erythritol-intercalated CNTs. The values of the steady-state temperature $T_s$ achieved are shown by the corresponding colors. For the experiments the inlet coolant temperature was 24.6 °C. The rectangular domains in the left-hand side panels corresponding to the steady-state regimes are shown in detail in the right-hand side panels.
Conclusion

The results show that wax-intercalated and erythritol-intercalated carbon nanotubes (CNTs) hold promise as phase change materials (PCM) for cooling microelectronics using coolant suspension flow in microchannels. CNTs were intercalated with wax using the method of self-sustained diffusion. Surfactant-stabilized aqueous suspensions of 1 wt% CNTs did not clog a 603 μm channel, whereas in a 1803 μm channel flows of suspensions of up to 3 wt% wax-intercalated CNTs were possible. The flow rates of such suspensions were in the range 5–55 ml min⁻¹. It was found that the presence of the surfactant NaDDBS in water led to an apparent slip at the channel walls, which enhanced the convective heat removal from a hot copper block, in which the microchannels with flowing aqueous coolant were embedded. The presence of wax inside CNTs additionally facilitated heat removal through the latent heat of wax fusion. Wax melted in the range 45–47 °C and this effect alone was responsible for the maximum temperature reduction of 1.9 °C. The heat removal due to wax melting is diminished at the highest flow rates, since the CNT residence time inside the 3.175 cm-long channel becomes too short for wax melting.

The presence of erythritol inside CNTs additionally facilitated heat removal through its latent heat of fusion in flows of the oil-based suspensions. The erythritol melted in the range 118–120 °C and this effect alone was responsible for the maximum temperature reduction of 3.2 °C in flows of the oil-based 1.5 wt% suspension of erythritol-intercalated CNTs. The present approach can be also used in the case of mixtures of different PCMs, e.g. wax and erythritol (separately in different CNTs, or together in the same CNTs) to widen the temperature range in some applications.

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