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Short communication

Thermally induced movement of micro particles observed on a rough surface: A novel observation and its implications for high throughput analysis and synthesis

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ABSTRACT

It is shown how droplets (20–30 μm) can be made to move by a thermal gradient created by a thermal tip. Materials used were solid at room temperature and were then made liquid by holding the environmental temperature above the melting point. A scanning thermal microscope (SThM) was employed to subject these droplets to a strong temperature gradient. The system was then cooled and the movement of the particle was assessed from a topographic image. It was shown how these materials could be manipulated, moved, mixed together and how their chemical state could be assessed by IR spectroscopy. The possibility of doing this on such a small scale opens up new possibilities for high throughput analysis and synthesis.

1. Introduction

The ability to manipulate materials using thermal tips actuated by a scanning probe microscope has been demonstrated in a number of contexts; the ability to pick up small quantities of materials by softening them using a heated tip then retracting it (thermally assisted nanosampling or TAN) [1–4], the ability to deposit material previously coated onto the tip (thermal dip-pen nanolithography) [5], the ability to pick up Femtogram quantities of one material and then study how that material interacts with another (nano-interaction studies) [1–3] and the ability to cause local chemical reactions to created nano-scale objects [6] have all been illustrated using a range of materials. It has also been shown how a thermal tip can be used for photothermal Fourier-transform infrared spectroscopy (PT-FTIR) [7–9], spectra of a localised region of a material can be acquired by placing the thermal tip in contact with the surface of a bulk sample while focusing the beam of an FTIR spectrometer at the point of contact. It is also possible to acquire spectra of material attached to the tip while it is remote from any surface. This latter measurement can be combined with TAN so that a sample can be taken from a selected point and then its chemical composition can be analysed.

A separate field of endeavour has been to cause the movement over a surface of small droplets; this has been achieved by controlled surface tension gradient [10,11], thermocapillary forces [12–14], pressure gradients [15], electrokinetic forces [16] or magnetohydrodynamic pumping [17]. Of relevance in the context of this letter is the work of Daniel et al., who reported the fast movement of liquid drops (about 1–2 mm diameter in air) on a surface with a radial temperature gradient that generates a surface tension-driven fluid motion [10]. Wasan et al. presented a simple model to estimate the maximum lateral velocity at the drop surface due to the surface tension gradient [11]. Darhuber et al. demonstrated the manipulation of liquid samples (polydimethyl-siloxane, dodecane, di(ethylene glycol) and water, around 2 mm diameter droplet) on chemically patterned surfaces by means of electronically addressable microheater arrays [12,13]. Chen et al. explored the physical mechanisms affecting thermocapillary migration of droplets generated by surface temperature gradient [14]. It should be noted that in all of these examples the droplets are of the order of millimetres and the movement is from the hotter region toward a colder one. The ability to move materials under computer control means highly parallel investigations can be carried out where materials are mixed so pos-

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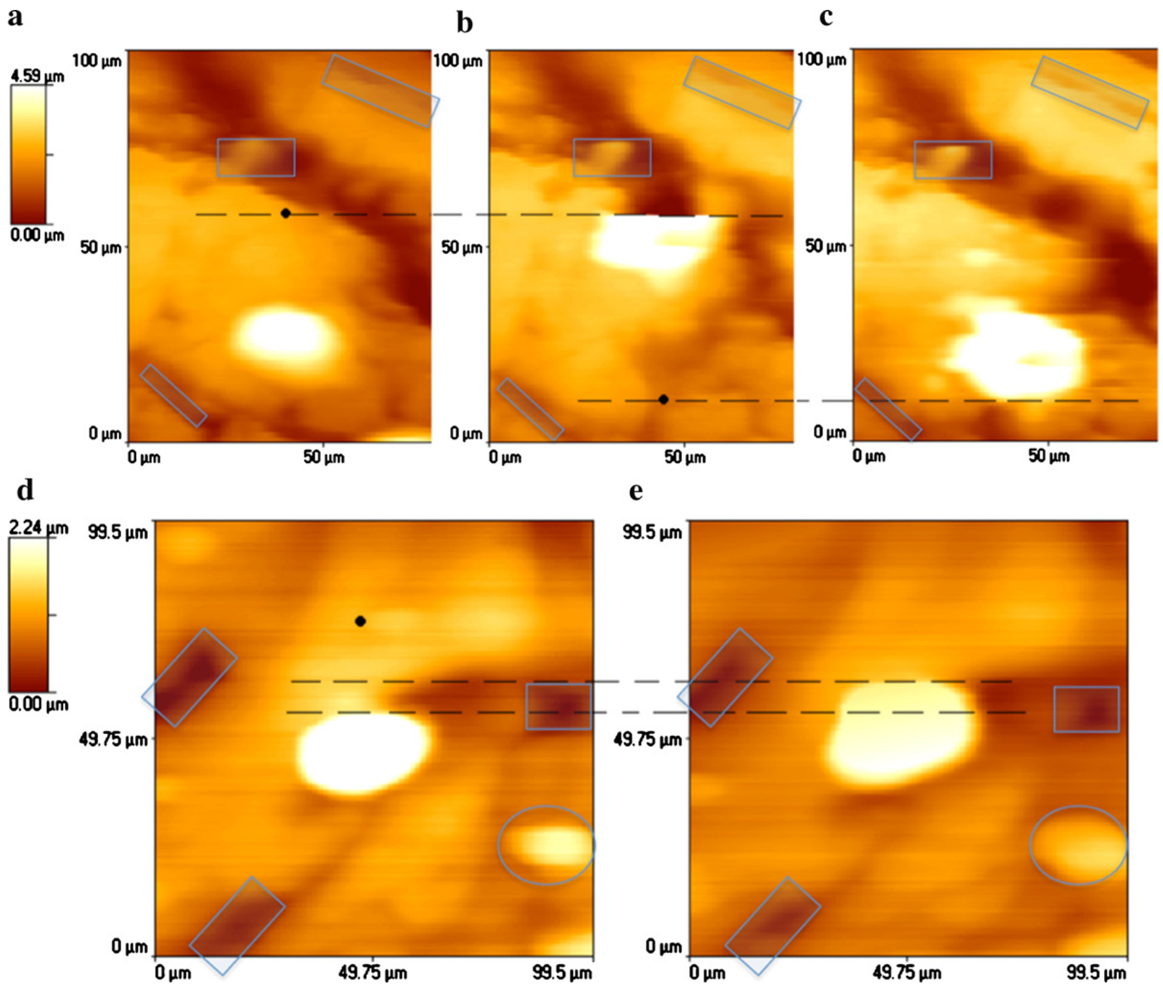

Fig. 1. AFM topography images of stearic acid before (a) and after (b) and again (c) applying the voltage. Black dot indicated the position of the probe and the rectangles indicating features that remain substantially invariant. And AFM topography images of glycerol dibehenate before (d) and after (e) applying the voltage, the rectangles indicate features that remain invariant while the circle indicates a particle that does not move.

sible interactions and chemical reactions can be investigated 'on a chip'.

In this study we report an unexpected discovery made while we attempted to explore the possibilities for manipulating droplets of the order of tens of microns in a strong thermal gradient created by a thermal tip. For the first time we show how droplets (20–30 µm) can be made to move by these thermal gradients. It is also shown for the first time how these materials can be manipulated, moved, mixed together and their chemical state assessed by IR spectroscopy.

2. Experimental

2.1. Materials and instrumentation

Glycerol dibehenate (Gattefosse, France, *mp* 78 °C) and stearic acid (Fluka, Gillingham, UK, *mp* 65 °C) were selected as the model materials and used as received.

Localised thermomechanical analysis and the voltage were performed using the Explorer^{TM} scanning probe microscope (SPM) (Veeco, CA) and Anasys Instruments temperature control hardware and software. Wollaston wire thermal probes (Veeco, CA) were used throughout the experiments [18,19]. Samples were fixed to the magnetic stub using double-sided tape and mounted onto an X-Y translating microscope stage. The stub was a standard mild steel sample stub supplied by Veeco; its root mean square roughness was determined to be 0.1984 µm by the image analysis software supplied by the manufacturer. Photothermal Fourier-transform infrared (PT-FTIR) microspectroscopy was set up by interfacing an IFS/66S spectrometer (Bruker Optics, Coventry, UK) with the Explorer SPM with a Wollaston wire thermal probe using optics described elsewhere [7].

2.2. Experimental procedure

The experimental procedure was as follows: particles of stearic acid or glycerol dibehenate were dispersed on the surface. The temperature of the stage was raised up to 80 °C at 10 °C/min. After the stage was cooled down to room temperature a particular particle which had adhered to the surface was selected and a topography image of the particle was obtained (Fig. 1a) to locate its position. The diameter of the particle was 20–30 µm. The probe was then moved to 20 µm away from the edge of the particle and the temperature of the stage was again increased to 80 °C. 3 V was applied to the Wollaston wire thermal probe for 1 s to generate a temperature gradient between the probe and the particle. After that, the stage was cooled down, thus solidifying the sample, and the probe was scanned over the same area to obtain a topographic image (Fig. 1b). The position of the probe during application of the temperature gradient is shown as a black dot in the figure.

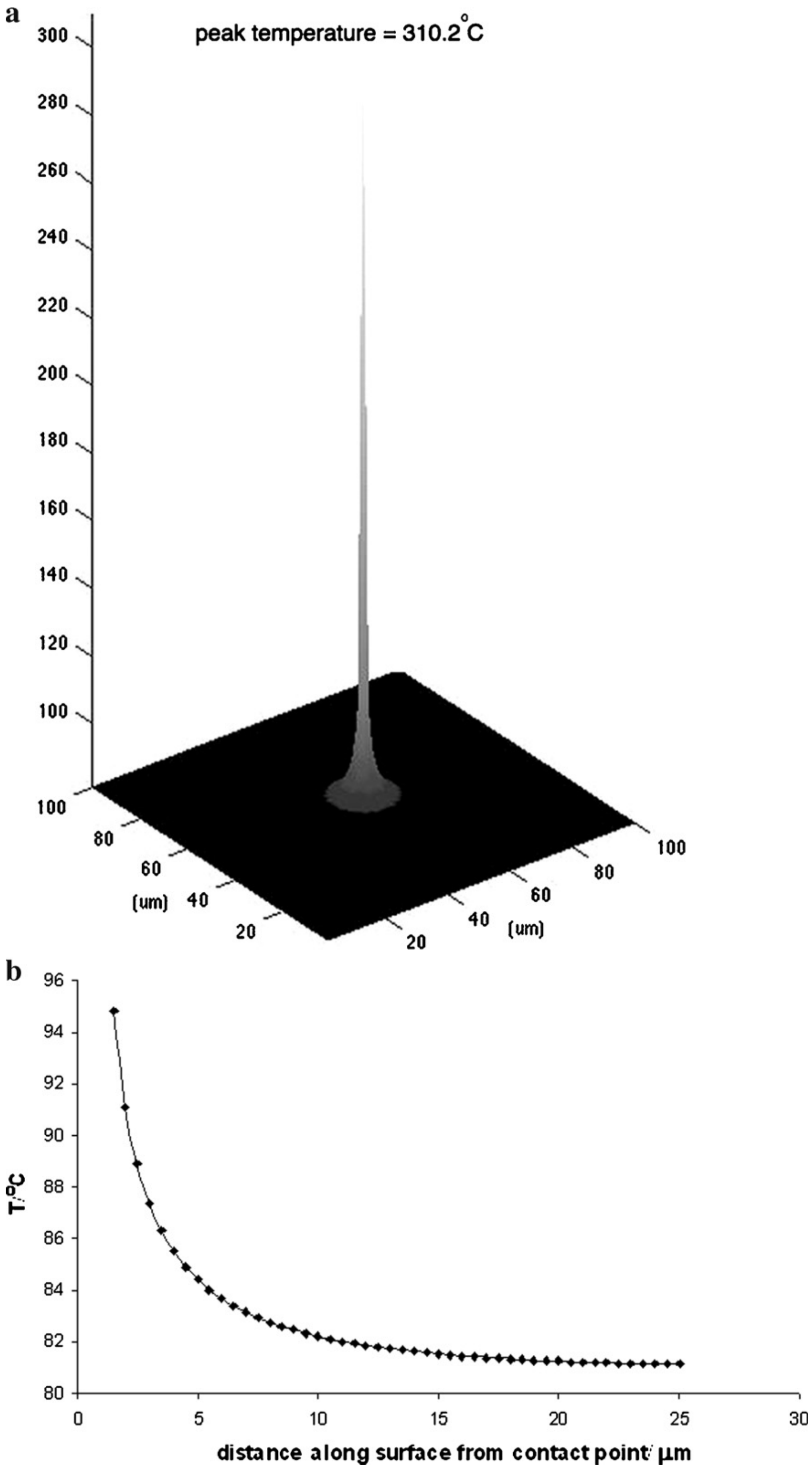

Fig. 2. Surface thermal profile (a) and temperature profile on the surface (b) from a numerical simulation using the transmission line matrix (TLM) technique.

3. Results and discussion

Our approach was to start with a solid particle. For simplicity we have used materials that are solid at room temperature which were made liquid by holding the environmental temperature above the melting point of the particle by the use of a hot stage. We then used a scanning thermal microscope (SThM) to subject these droplets to a strong temperature gradient. The system was cooled to cause the material to again become solid, after this any movement of the particle was assessed using the SThM simply as an AFM to acquire an image of topography in contact mode. By applying a voltage to the tip it heated a point on a surface in a highly localised manner. For this experiment we used low molecular weight organic compounds, so that they would have low viscosity above their melt-

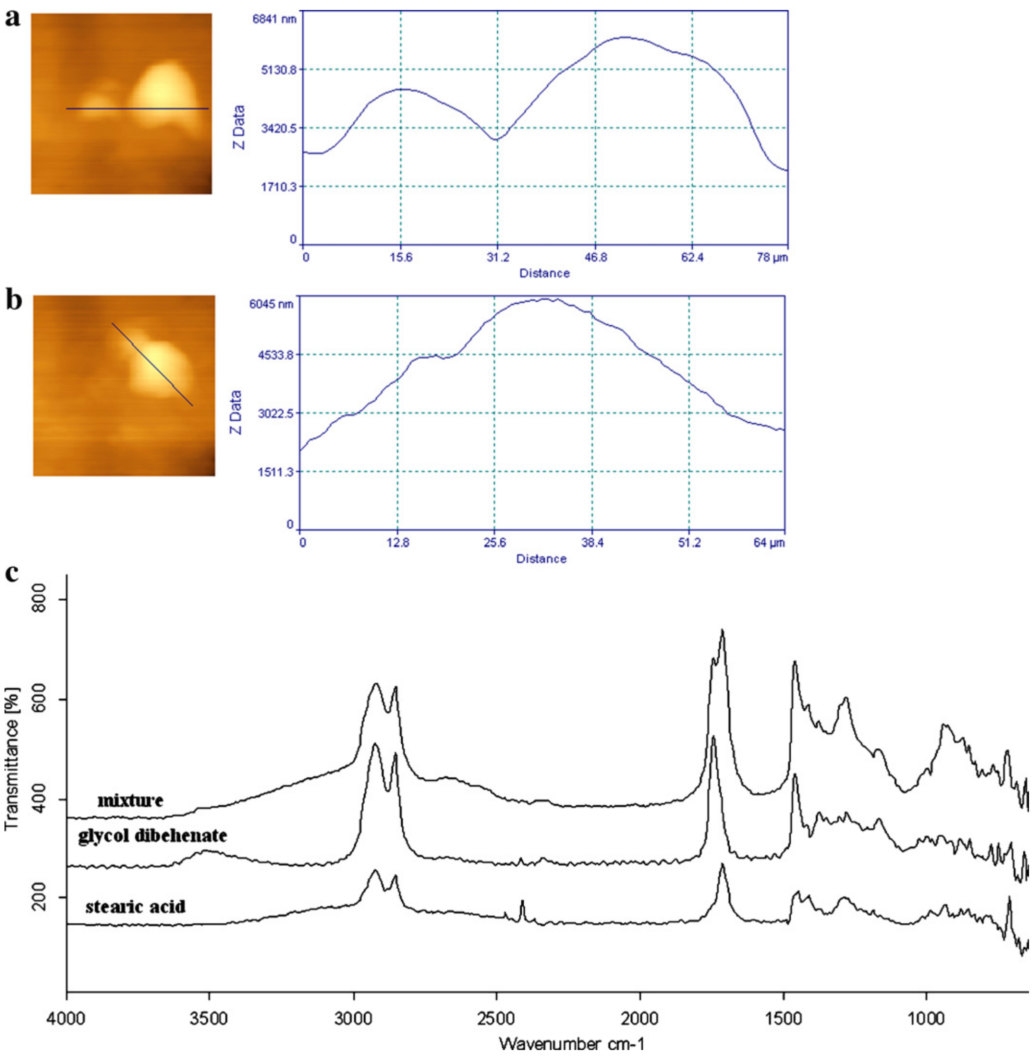

Fig. 3. AFM topography images and line measurements of the mixture particles before (a) and after (b) applying the voltage; (c) photothermal Fourier-transform infrared microspectroscopy infrared spectra of glycerol dibehenate, stearic acid and the mixture, resolution of 8 cm^{-1}, from 4000 cm^{-1} to 500 cm^{-1}, for 100 scans.

ing points and also relatively low melting point well below their decomposition temperature to give a large temperature window in which to operate.

A number of different smooth surfaces were explored including stainless steel mirrors, gold foil and gold coated mica. On none of these was particle motion observed in any consistent manner. In order to negate any effects of high thermal conductivity we also used glass slides again without effect. Only in one case, that of a rough stainless steel surface was motion consistently observed. All of the experiments were carried out using the same Wollaston wire probe. The results presented in Fig. 1a to c showed how a particle can be made to move in one direction and then its motion was reversed by relocating the tip. In this experiment, the sample of stearic acid moved 20 μm toward the heated tip on both occasions. The same experiment was performed using a particle of glycerol dibehenate which moved approximately 6 μm toward the probe, which was shown in Fig. 1d and e. Repeat experiments established that the amount of movement from the two materials caused by applying a temperature gradient for 1 s was 20 μm ± 1.2 μm for the stearic acid and 6 μm ± 0.5 μm for the glycerol dibehenate. Repeating the same procedure without applying the thermal gradient, no particle movement was observed for either stearic acid or glycerol dibehenate. These experiments were challenging because heating and cooling the sample inevitably caused some mechanical drift to occur. Furthermore the material was heated above its melting temperature and then cooled so the shape of the particles might change or even their position might change as a consequence of vibrations when the sample was fluid. To address the question of drift, features that remained invariant from image to image were indicated by rectangles in all of the images in Fig. 1. Measurements of the apparent movement of the centres of these features relative to one another indicate the drift was of the order of 0.5 μm thus the observed movement of the particles in the images shown in Fig. 1 was one to two orders of magnitude greater than the drift. In images 1d and e a circle indicated a particle that did not move its centre of mass (although some changes in shape were caused by the heating and cooling cycle) while the bigger particle nearer the heated tip did thus illustrating how proximity to the heated tip was the governing factor in determining whether a particle moved significantly or not.

When the thermal conductivity of the substrate approaches that of the heating element of the thermal probe, as in this case, the usual calibration procedure based on standard organic samples with known melting points cannot be used [20]. Because of this and because we had no way of measuring the thermal gradient as a consequence of the fact the same tip cannot heat at a point and measure the temperature elsewhere we resorted to a numerical simulation. The heating effect of the probe was investigated by considering a transmission line matrix (TLM) model [21] where the hot probe-tip (a wire described using a cylindrical polar mesh) was brought into contact with the surface of the substrate described using a three-dimensional Cartesian mesh. Spatial discretisations were arranged so that heat was exchanged across a single nodal interface, where thermal continuity was assumed. The TLM technique has particular advantages over alternatives such as finite element simulations when modelling materials with disparate thermal properties. The material properties used for the model were as follows: for the stainless steel stub, density 7750 kg/m^3, specific heat 500 J/kg K and thermal conductivity 16 W/m K. For the platinum tip density 21,450 kg/m^3, specific heat 130 J/kg K and thermal conductivity 72 W/m K. The contact area between the tip and stub was taken to be 0.5 μm × 0.5 μm. A series of numerical experiments indicated that temporal discretisations of 10 ns was required in order to minimise errors for a spatial discretisations of 0.5 μm. The model was then run from the instant of contact until steady-state was reached. The resultant surface thermal profile and temperature profile on the surface are shown Fig. 2. Further details on the TLM technique and its application to thermal modelling can be found in [21].

The electrical resistance between the thermal tip and the steel stub was investigated using a standard Ohmmeter (328 digital multimeter from Rapid Tools) and was found to be an open circuit. The small contact area and the presence of oxide layers must mean that there was effectively no electrical connection between the probe and the substrate; this and the high electrical conductivity of the substrate means that electric potential gradient can be ruled out as a possible cause of the particle movement.

A point that should be noted is that, in contrast to the previous studies that have shown that thermal gradients can cause materials to move; in both of the examples cited here the droplet moves from the colder region to the hotter one, it also occurs only on a rough surface. This may be due to the special effects that a rough surface can have on surface tension [22]. Persson [23] has proposed that the fractal nature of rough surfaces and its impact on the properties of the frozen capillary wave (that is produced in both the processes he considered and in our experiment) could explain the anomalous sheer stress behaviour of glassy polymer lenses. Similar arguments might apply to the systems we have investigated but this is necessarily highly speculative as our experiment incorporates that added complexity of a thermal gradient. It is hoped that the surprising observation that has been made will prompt further investigations. The lack of any movement on any of the smooth surfaces investigated would point to roughness-induced effect.

Having established that droplets can be caused to move using the thermal tip, we investigated the possibility of causing two materials to combine by using thermally assisted sampling. Two particles, one of stearic acid and the other of glycerol dibehenate, were deposited next to each other. Then they were caused to move together by the action of a thermal gradient, which was illustrated in Fig. 3a and b. Furthermore, we have shown that the composition of such a combined particle can be interrogated by a combination of thermally assisted nanosampling and photothermal spectroscopy. In Fig. 3c the spectrum of the combined particle is clearly a combination of the spectra of the two separate materials. In this case no chemical interaction between the two materials was detected or expected but it can easily be seen how materials could be manipulated and added together and analysis of the chemistry of reactions between them could all be effected and analysed by a thermal tip either singly or in an array. In the examples given here nanogram quantities of sample were used. However, thermal tips have already been used for materials manipulation of and even the analysis by spectroscopy of femtogram quantities and we expect the principles we have demonstrated here could be applied on this scale when suitable probes become available. Furthermore, the mobile tip could be replaced by an array of stationary heaters/sensors which could achieve the same things. Here we have used molten materials for convenience but it is possible to envisage that solutions could be used, most materials can be made solid by cooling thus the experiment described here could be extended to cover a wide range of substances. Here we have used contact mode AFM to locate the droplets and measure their movement but an array of thermal sensors could detect the location and movement of droplets by using an AC modulation of the heater to measure the local heat capacity which could provide a sensitive measure of the presence or absence of a droplet on a sensor.

4. Conclusions

In a summary, we showed in this study how droplets (20–30 μm) can be made to move by a thermal gradient created by a thermal tip. The location of the droplet and its movement were clearly visualised with AFM images. The thermal gradient between the droplet and the probe was simulated using a numerical model to understand the condition of the droplet, the probe and the metal surface. It was also shown how these materials can be manipulated, moved, mixed together and their chemical state assessed by IR spectroscopy.

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