

Localized Joule heating produced by ion current focusing through micron-size holes

V. Viasnoff,^{1,a)} U. Bockelmann,¹ A. Meller,² H. Isambert,³ L. Laufer,⁴ and Y. Tsori⁴

¹Nanobiophysics Laboratory, ESPCI, CNRS, 10 rue Vauquelin, 75005 Paris, France

²Department of Physics and Biomedical Engineering, Boston University, Boston, Massachusetts 02215, USA

³Institut Curie, CNRS, 11 rue P.M. Curie, 75005 Paris, France

⁴Department of Chemical Engineering, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel

(Received 14 December 2009; accepted 24 March 2010; published online 19 April 2010)

We provide an experimental demonstration that the focusing of ionic currents in a micron size hole connecting two chambers can produce local temperature increases of up to 100 °C with gradients as large as 1 °K μm^{-1} . We find a good agreement between the measured temperature profiles and a finite elements-based numerical calculation. We show how the thermal gradients can be used to measure the full melting profile of DNA duplexes within a region of 40 μm . The possibility to produce even larger gradients using submicron pores is discussed. © 2010 American Institute of Physics. [doi:10.1063/1.3399315]

The creation of local heat sources and large thermal gradients in confined aqueous environments is a challenging problem due to the rapid diffusion of heat in water. Several solutions were proposed, such as heating micro/nanoparticles^{1,2} by magnetic induction or by using a focused laser beam.^{3,4} Local thermal gradients in microchannels were used to sort and concentrate molecules. Several approaches were developed such as thermophoresis,⁵ temperature gradient focusing,⁶ field gradient focusing,⁷ and isoelectric focusing.^{8,9} These techniques use high dc voltages (tens to hundreds of volts) and thermal gradients in the range of 0.01 °K μm^{-1} . The typical volumes are micro to nanoliters. In this paper, we show that a few tens of picoliters can be strongly heated by focusing an ionic current through a micron size hole in a saline solution. The resulting gradients are of the order of 1 °K μm^{-1} .

We use a custom made cell composed of two chambers separated by a 50 μm thick Teflon septum (see Fig. 1). A conical hole (40° half angle, minimum diameter $r_0 = 7.5 \mu\text{m}$) is punctured in the center of the septum. The ac voltage ($\approx 100V_{pp}$, 10 kHz) is applied across the chambers using platinum electrodes. We use tris buffer, 1 M KCl, pH 7.4, of electrical conductance $\sigma = 107 \text{ mS/cm}$. The dc value of the electrical resistance R_h across the hole is 2300 Ω . The septum capacitance is estimated to $C_s = 0.4 \text{ pF}$. It results that the current across the chambers is mostly resistive at 10 kHz. The Joule heating power P_j dissipated in the hole is proportional to the mean root square current i_{rms} . We measure the local temperature profiles along the vertical hole axis in the lower chamber. The temperature is derived from the confocal detection ($\lambda = 532 \text{ nm}$) of the calibrated fluorescence of tetramethylrhodamine (TMR) grafted at the 5' end of DNA oligomers.

Large enough currents $i_{\text{rms}} > 1.9 \text{ mA}$, results in buffer vaporization. Smaller values of i_{rms} lead to stationary thermal profiles within a few seconds. Figure 2(a) shows the temperature increase $\Delta T = T - T_\infty$, where $T_\infty = 298 \text{ °K}$ is the room temperature, along the vertical axis for $i_{\text{rms}} = 1.81 \text{ mA}$. Over the first 40 μm , the average temperature gradient is

1 °K μm^{-1} . As a first approximation we model the heating power P_{eff} as being distributed uniformly in an effective sphere of radius r_{eff} . The temperature then reads as follows:

$$\Delta T(r) = \frac{P_{\text{eff}}}{8\pi\kappa r_{\text{eff}}} \left(3 - \frac{r^2}{r_{\text{eff}}^2} \right) \quad r < r_{\text{eff}},$$

$$\Delta T(r) = \frac{P_{\text{eff}}}{4\pi\kappa r} \quad r \geq r_{\text{eff}}, \quad (1)$$

where r is the distance from the hole center and $\kappa = 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ is the thermal conductivity of water. Figure 2(a) shows the measured temperature profile for hole radius $r_0 = 7.5 \mu\text{m}$ and power $P_j = 6.5 \times 10^{-3} \text{ W}$. The best fit parameters for our model are $r_{\text{eff}} \approx 17.8 \mu\text{m}$ and a $P_{\text{eff}} = 5.2 \times 10^{-3} \text{ W}$. This model predicts that when $r > r_{\text{eff}}$ the value of $(r/r_0)\Delta T(r)/\Delta T(r_0)$ is a constant independent of r_0 and P_j . Figure 2(b) shows that the experimental curves can be scaled this way for several values of r_0 and P_j provided that we take $r_{\text{eff}} = 2.4r_0$.

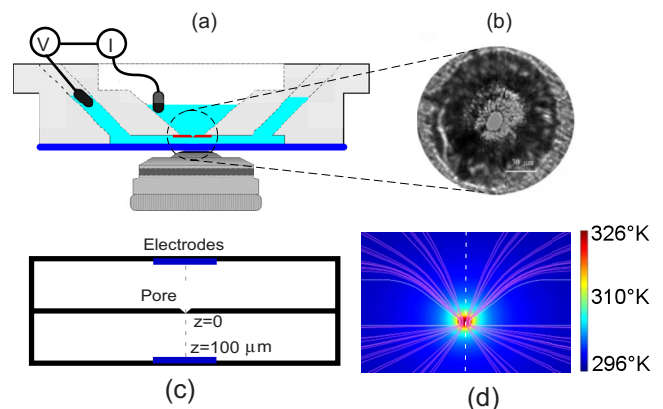


FIG. 1. (Color online) (a) Schematic representation of the experimental setup. The two chambers are separated by a 50 μm thick Teflon septum punctured by a 7.5 μm radius conical hole (b) Close up on the hole region. (c) Model set up used for our finite element modeling. (d) Close up on the pore region. The ion current lines are represented and the map of the temperature profile is color coded.

^{a)}Electronic mail: virgile.viasnoff@espci.fr.

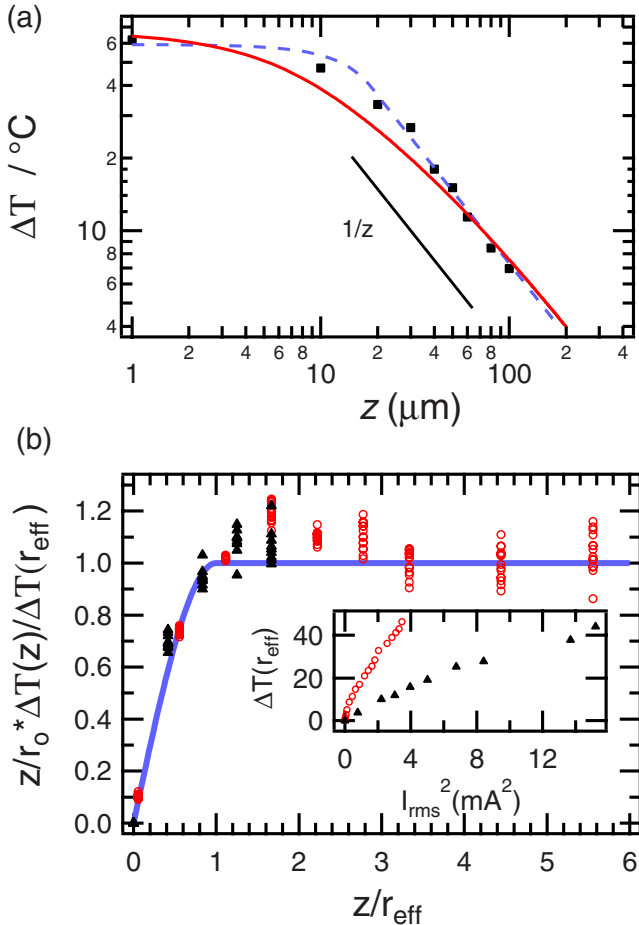


FIG. 2. (Color online) (a) Profile of the temperature increase $\Delta T(z)$ along the vertical axis below the hole center. The pore's radius is $7.5 \mu\text{m}$ and the current is $i_{\text{rms}}=1.81 \text{ mA}$. The average thermal gradient over the first $40 \mu\text{m}$ is $1^\circ\text{K} \mu\text{m}^{-1}$. At distances larger than the hole radius the temperature profiles $\Delta T(z)$ scale as $1/z$. The dotted line is the fit obtained when modeling the heating source by a spherical source of uniform heating power $P_j=5.2 \times 10^{-3} \text{ W}$ and radius $r_{\text{eff}}=17.8 \mu\text{m}$. The solid line is the finite element calculation. (b) Rescaling of all temperature profiles obtained with a hole of $7.5 \mu\text{m}$ (open circles) and $20 \mu\text{m}$ (full triangles) for various currents ($0.5 \text{ mA} < i_{\text{rms}} < 1.85 \text{ mA}$). We used $r_{\text{eff}}=2.4r_0$. The straight line corresponds to the scaling of the analytical model. Inset: Values of $\Delta T(r_{\text{eff}})$ as a function of I_{rms} for the hole of $7.5 \mu\text{m}$ (open circles) and $20 \mu\text{m}$ (full triangles).

In order to explore the influence of the pore geometry on thermal profiles we use a finite elements approach with various hole radiuses r_0 and pore lengths L . The numerical calculation accounts for mass transport (2), electrostatic potential (3), and heat dissipation (4) in the following way:

$$\partial_t C^\pm - \nabla(D^\pm \nabla C^\pm \pm e z \mu^\pm C^\pm \nabla \phi) = 0, \quad (2)$$

$$\partial_t(\nabla(\epsilon \nabla \phi) + \nabla(\sigma \nabla \phi)) = 0, \quad (3)$$

$$\rho C_p \partial_t T - \nabla(\kappa \nabla T) - \sigma(\nabla \phi)^2 = 0, \quad (4)$$

C^\pm , D^\pm , and μ^\pm are the number densities, the diffusion coefficients, and the electrophoretic mobilities of the positive and negative ions, respectively. ϕ is the electric potential, ϵ is the local dielectric constant, σ is the electrical conductivity, e is the electron's charge, and C_p is the heat capacity. The steady-state solutions were obtained with an ac voltage at the electrodes.¹⁶

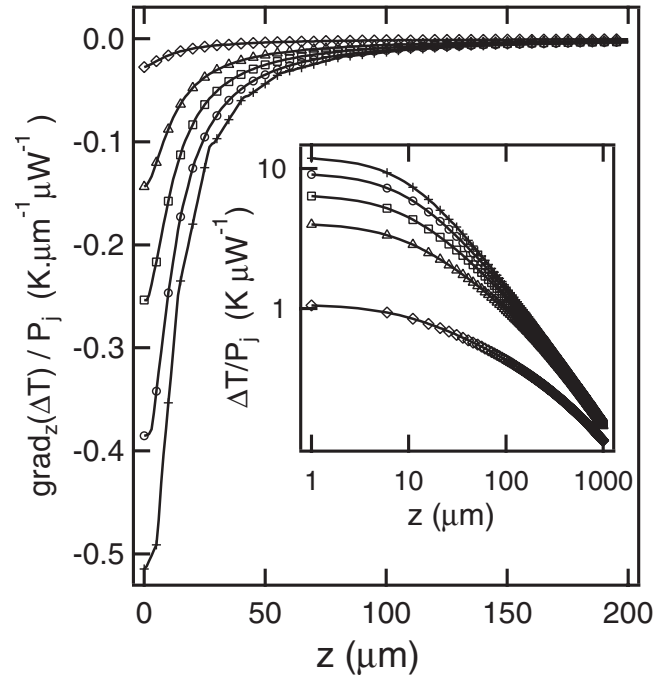


FIG. 3. Steady state temperature gradients and profiles (inset) below the narrowest constriction of the hole given by finite elements calculation. $\nabla_z T(z)$ and $\Delta T(z)$ are scaled by the average heating power P_j for various ratios of hole size $r_0=10 \mu\text{m}$ with the membrane thickness L . The values of r_0/L are 0.01 (\diamond), 0.05 (\triangle), 0.1 (\square), 0.2 (\circ), and 0.5 ($+$). $\Delta T(z)$ agrees with Eq. (1) and decays like z^{-1} at $z > r_0$ for r_0/L larger than 0.1 . For lower ratios the thermal gradients are less steep.

Figure 3 shows the calculated temperature $\Delta T(z)$ and gradient profiles $\nabla_z T(z)$ along the z axis at a fixed heating power P_j for several values of the aspect ratio r_0/L . When $r_0/L > 0.1$ the temperature is well described by $\Delta T(z) \sim z^{-1}$ for z values larger than $2r_0$. In the limit of small aspect ratio the heating is mainly localized in the hole and smoothly spreads in the lower chamber producing smaller temperature gradients. We conclude that r_0/L should ideally be between 0.1 and 1 to obtain the sharpest gradients and largest temperature increases.

The experimental thermal gradients generated by a hole of diameter $r_0=20 \mu\text{m}$ are used to determine the melting profile a DNA duplex: strand 1: TMR 5'-TCAGACCG(TC)₁₅-3', strand 2: 5'-CGGTCTGA-3' IowaBlack. The DNA was gel purified to obtain a 95% hybridization efficiency. The fluorescence intensity of the TMR is quenched 20-fold on average upon hybridization with IowaBlack. With a proper baseline calibration the fluorescence intensity measured at the laser spot can be used to determine the fraction of hybridized duplexes. We measure the fluorescence profiles at various values of i_{rms} for strand 1 only, and for the hybridized duplex with a 1:1 ratio of both strands (see Fig. 4). Assuming (i) a local thermal equilibrium, (ii) a two state model where the eight mers are either fully hybridized or completely open, and (iii) an efficient quenching for all temperatures, we can extract the dissociation coefficient α of the hairpin as a function of temperature and distance from the pore. Figure 4 shows the full melting profile obtained over a distance of $45 \mu\text{m}$ for a hole of radius $r_0=20 \mu\text{m}$. Following the typical melting curve analysis for bimolecular equilibrium,¹⁰ we extract the thermodynamical melting parameters of the DNA structure. We

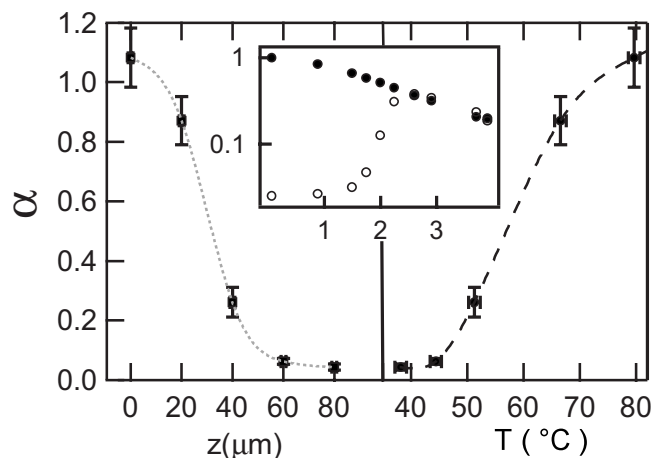


FIG. 4. The dissociation ratio $\alpha \equiv I_{\text{fluo}}(\text{DNA} + \text{quencher}) / I_{\text{fluo}}(\text{DNA only})$ as a function of distance and temperature for $i_{\text{rms}} = 2.9$ mA. A decrease of 90% is obtained over 45 μm or 35 $^{\circ}\text{C}$. The hole diameter is 40 μm . Inset: Fluorescence intensity as a function of the ionic current for a single DNA strand labeled with TMR only (full symbol) and a DNA duplex with TMR quenched with IowaBlack (open symbol). The lines are guides to the eyes.

find $\Delta H = -66 \pm 6$ kcal mole $^{-1}$ and $\Delta S = 182 \pm 25$ Cal mole $^{-1}$ K $^{-1}$, in good agreement with the thermodynamical parameters calculated with MFOLD (Ref. 11) under similar salt conditions ($\Delta H = -62$ kcal mole $^{-1}$ and $\Delta S = 169$ Cal mole $^{-1}$ K $^{-1}$). Spatial temperature gradients have the advantage over traditional melting curves techniques that all temperatures can be probed simultaneously. This method works if the diffusion and/or drift of the DNA molecule across the thermal profile is slow enough to allow thermal equilibration. As derived in Ref. 16, electrophoretic, and electro-osmotic drifts are negligible in our experiments. The Brownian diffusion coefficient¹² for our DNA molecules is of order $D_{\text{DNA}} \approx 10^{-7}$ cm 2 s $^{-1}$. The distance over which the temperature changes by 1 $^{\circ}\text{C}$ is $d = 1$ μm . The diffusion time across this distance is $\tau = d^2 / D_{\text{DNA}} = 0.01$ s. Since small molecular beacons are reported to open over a characteristic time of 10^{-4} s,¹³ the approximation of local equilibrium is satisfied.

We briefly discuss the influence of various parameters on the applicability of our device. For frequencies

$\omega < (R_h C_s)^{-1} = a r_0^2 / (\sigma C_s)$, where a is a geometry-dependent factor, the ionic current is mostly resistive. It is reasonable to assume that electro-osmotic flow are negligible due to the use of ac fields. Electro-osmosis can be significantly enhanced in smaller (≈ 100 nm) or charged pores when current rectification occurs.¹⁴ In the lower chamber natural convection is minimized since the hot spot (the hole) is located above the cold region. In addition, there is negligible fluid transfer between the upper and lower chambers. The small extent of the lower chamber also increases the instability threshold for natural convection. This situation contrasts with focused laser heating for which convective rolls are observed along the optical axis.⁴ Convection can be externally applied to drive the molecule through the thermal profile. Our conclusions would still hold in the limit of small Peclet numbers, i.e., if the convective velocity is small: $v < \kappa / \rho C_p r_0 = 10^{-5} / r_0$ m s $^{-1}$. In this limit thermal quenching rate of 1 $^{\circ}\text{K} / \mu\text{s}$ can still be achieved.¹⁶ We believe that this approach facilitates the creation of large thermal gradients in submicron regions with potential applications for fast denaturation and thermal quenching¹⁵ to study local chemical reactions.

¹K. Hamad-Schifferli, J. J. Schwartz, A. T. Santos, S. G. Zhang, and J. M. Jacobson, *Nature (London)* **415**, 152 (2002).

²M. Lévy, C. Wilhelm, J. M. Siaugue, O. Horner, J. C. Bacri, and F. Gazeau, *J. Phys.: Condens. Matter* **20**, 204133 (2008).

³P. Baaske, S. Duhr, and D. Braun, *Appl. Phys. Lett.* **91**, 133901 (2007).

⁴D. Braun and A. Libchaber, *Phys. Rev. Lett.* **89**, 188103 (2002).

⁵S. Duhr and D. Braun, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 19678 (2006).

⁶D. Ross and L. E. Locascio, *Anal. Chem.* **74**, 2556 (2002).

⁷W. S. Koegler and C. F. Ivory, *Biotechnol. Prog.* **12**, 822 (1996).

⁸J. Pawliszyn and J. Q. Wu, *J. Microcolumn Sep.* **5**, 397 (1993).

⁹B. Kates and C. L. Ren, *Electrophoresis* **27**, 1967 (2006).

¹⁰J. L. Mergny and L. Lacroix, *Oligonucleotides* **13**, 515 (2003).

¹¹Mfold online server: <http://www.bioinfo.rpi.edu/applications/mfold>.

¹²B. Tinland, A. Pluen, J. Sturm, and G. Weill, *Macromolecules* **30**, 5763 (1997).

¹³G. Bonnet, O. Krichevsky, and A. Libchaber, *Proc. Natl. Acad. Sci. U.S.A.* **95**, 8602 (1998).

¹⁴Z. Siwy, *Adv. Funct. Mater.* **16**, 735 (2006).

¹⁵V. Viasnoff, A. Meller, and H. Isambert, *Nano Lett.* **6**, 101 (2006).

¹⁶See supplementary material at <http://dx.doi.org/10.1063/1.3399315> for a detailed discussion of the approach limitations.