Thermal transpiration in zeolites: A mechanism for motionless gas pumps

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We explore the use of a naturally occurring zeolite, clinoptilolite, for a chip-scale, thermal transpiration-based gas pump. The nanopores in clinoptilolite enable the required free-molecular flow, even at atmospheric pressure. The pump utilizes a foil heater located between zeolite disks in a plastic package. A 2.3 mm thick zeolite disk generates a typical gas flow rate of 6.6×10^{-3} cc/min-cm^2 with an input power of $<300\ \mathrm{mW/cm^2}$. The performance is constrained by imperfections in clinoptilolite, which provide estimated leakage apertures of 10.2–13.5 $\mu\mathrm{m/cm^2}$ of flow cross section. The transient response of the pump is studied to quantify nonidealities. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3025304]

Interest in portable handheld gas sensing microsystems, such as breath analyzers, gas chromatographs, and warfare agent detectors, has motivated research in gas micropumping technology for more than two decades.[1–3] These research efforts have explored micropumps based on different actuation techniques such as electrostatic, piezoelectric, etc., which continue to evolve with respect to drive voltage requirements, reliability, and complexity.[4,5] Most micropumps have moving parts which adversely affect their scalability. With miniaturization, moving parts experience relatively higher frictional losses due to an increased ratio of surface area to volume. This letter focuses on the use of a naturally occurring zeolite in a thermal transpiration-driven Knudsen pump. Knudsen pumps have the promise of high reliability because they have no moving parts and no operating fluids, which eliminate some of the potential sources of failure.

Naturally occurring zeolites have a dense interconnected network of nanochannels ($>10^{14}$ pores/cm^2). These billions of nanochannels can transpire gas in unison, resulting in gas flow rates significantly greater than possible with a microfabricated Knudsen pump having a limited number of lithographically patterned nanochannels. Clinoptilolite, the zeolite used in this study, is one of the most abundant and widely mined natural zeolites, and is easily machinable. It has nanopores with hydraulic diameter of ≈ 0.45 nm and has bulk porosity of $\approx 34\%$.[6] It is an inexpensive, easily accessible, and mechanically strong nanoporous material.

Thermal transpiration refers to the phenomenon of gas molecules drifting from the cold end to the hot end of a narrow channel subjected to a longitudinal temperature gradient.[7] Reynold's pioneering investigations of thermal transpiration were closely followed by a rigorous mathematical analysis by Maxwell in 1879.[8,9] In 1910, Knudsen first proposed the feasibility of a gas pump based on this phenomenon.[10]

Although the phenomenon of thermal transpiration has been known for more than a century, very few efforts have focused on the atmospheric pressure operation of a Knudsen pump because this requires channels with hydraulic diameter smaller than approximately 100 nm. Vargo and Muntz reported a mesoscale device for operation near atmospheric pressure using nanoporous aerogel, providing a best case pressure drop of 11.5 Torr ($\approx$1.5 kPa) using helium.[11] McNamara and Gianchandani reported the feasibility of using lithographically patterned nanochannels in a chipscale, fully micromachined, Knudsen pump that achieved a pressure drop of about 54.7 kPa with 80 mW of input power.[12] However, the limitation on the density of lithographically patterned narrow channels in a micromachined Knudsen pump constrains the flow rate to the order of 10^{-6} cc/min.

Narrow channels, required for the thermal transpiration, are characterized by a Knudsen number (Kn) greater than 0.1. The Knudsen number is defined as the ratio of the mean free path of the gas molecules to the hydraulic diameter of the channel. Gas flow through a channel can be categorized into different gas flow regimes, which include free molecular, transitional, slip, and viscous, corresponding to $\mathrm{Kn}>10$, $10>\mathrm{Kn}>0.1$, $0.1>\mathrm{Kn}>0.01$, and $\mathrm{Kn}<0.01$, respectively.[13]

Figure 1 illustrates the basic concept of a Knudsen pump. Consider two chambers, maintained at different temperatures (T_H and T_C) that are connected by a narrow channel that restricts gas flow to the free-molecular regime. If the system is sealed, the ratio of equilibrium pressures in the two chambers, P_H and P_C, is nominally given by the ratio of the square root of respective temperatures,

$$\frac{P_H}{P_C} = \left[\frac{T_H}{T_C}\right]^{1/2}. \tag{1}$$

For a channel with larger diameter that is in the slip flow regime, equilibrium must be achieved between two opposing flow fields, thermal creep flow and Poiseuille flow.[14] The former is the temperature gradient-driven transpiration of gas molecules along the channel walls, from the cold end to the hot end. The longitudinal pressure gradient along the channel

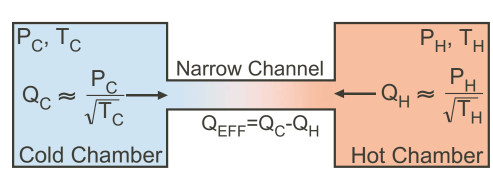

FIG. 1. (Color online) Thermal transpiration. If two chambers are connected by a channel that restricts flow to the free-molecular regime, the ratio of pressures at equilibrium is nominally equal to the ratio of the square root of their absolute temperatures.

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drives the Poiseuille flow in the central region of the channel, which acts to nullify the thermal creep flow.

If the chambers are not sealed, there is a continuous movement of gas molecules along the channel. The effective mass flow along a channel subjected to a temperature gradient can be estimated by Sharipov's model.[15] This model is based on a set of temperature and pressure flow coefficients that are numerically evaluated for a wide range of Knudsen numbers, which makes it applicable to practically all flow regimes. According to this model, the average thermal transpiration-driven gas flow rate along a channel is

$$\dot{M}_{\mathrm{av}} = \left[Q_T \frac{T_H - T_C}{T_{\mathrm{av}}} - Q_P \frac{P_H - P_C}{P_{\mathrm{av}}} \right] \frac{\pi a^3 P_{\mathrm{av}}}{l} \left[\frac{m}{2k_B T_{\mathrm{av}}} \right]^{1/2}, \quad (2)$$

where m, T_{av}, and P_{av} are the mass, average temperature, and average pressure of the gas molecules in the narrow channel, k_B is the Boltzmann constant, a and l are the hydraulic radius and the length of the narrow channel, and Q_P and Q_T are the pressure and temperature coefficients that depend on the rarefaction parameter δ_{av}, respectively, which can be expressed in terms of the collision diameter D of the gas molecules as

$$\delta_{\mathrm{av}} = \left[\frac{\pi^3}{2} \right]^{1/2} \frac{aD^2 P_{\mathrm{av}}}{k_B T_{\mathrm{av}}}. \quad (3)$$

Despite its relative simplicity, Sharipov's model is one of the most representative models for thermal transpiration-driven gas flow in submicron-sized channels. Various analytical and semianalytical models, as well as the computationally intensive direct simulation Monte Carlo technique have been benchmarked in this context in Ref. 16.

A semianalytical model is used to analyze the transient response of the Knudsen pump and its dependence on various nonidealities. Estimating the temporal evolution of pressure in the hot chamber requires the accommodation of physical nonidealities and this is done with the help of empirically fitted coefficients. In particular, these include (a) an equivalent leakage aperture associated with imperfections in the zeolite, which is responsible for the viscous, pressure-driven (Poiseuille) backflow of gas; and (b) the time constants for the heating and cooling of the structure, which determine the rate of thermal expansion and contraction of the gas, and thereby contribute to transient flows when the pump is switched on or off. It is worth noting that the gas flow will also be affected by parasitic heating of the cold chamber.

The zeolite-based Knudsen pump that we report here has two circular zeolite disks with a flexible heater sandwiched between them (Fig. 2). Thin, perforated aluminum disks are used on both sides of the zeolite disks to improve the temperature uniformity along these surfaces without blocking the gas flow. The assembly is packaged in a thermally insulating polyvinyl chloride (PVC) cavity. The two zeolite disks are peripherally bonded to the cavity using a vacuum grade epoxy (STYCAST 2850FT/Catalyst 9) to prevent leakage. The common outlet to both sides of the pump is located at the center, and the two inlets are at the top and the bottom of the device. This particular configuration, with a separate zeolite disk pumping gas from either side of a single heater, is termed the double-sided pumping architecture. (A single-sided pump, using just one zeolite disk, e.g., zeolite-1 in Fig. 2, is also possible.)

Figure 3 shows a fabricated device which has a final packaged volume of $55 \times 55 \times 12$ mm^3. It uses two 2.3 mm thick, 48 mm diameter zeolite disks, and a flexible resistive Kapton heater (18.7 Ω). The heater is a thin, etched-foil resistive element laminated between insulating layers of Kapton (Minco, MN).

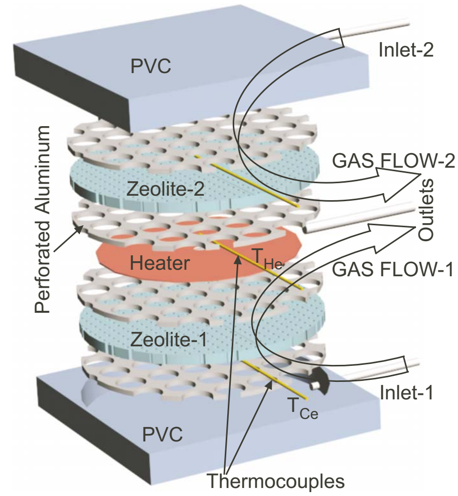

FIG. 2. (Color online) Exploded view of a zeolite-based Knudsen pump showing relative location of various components. The arrows represent the flow of pumped gas.

The equivalent leakage aperture due to imperfections in the natural zeolite samples is estimated by measuring the resistance to isothermal pressure-driven flow. The difference between the measured pressure and the ideal value for the nanoporous material [Eq. (2)] indicates the leakage (Poiseuille) flow (Fig. 4). Our 1.15 mm thick zeolite samples have typical leak aperture diameters of 10.2–13.5 μm/cm^2.

The Knudsen pumping characteristics of the devices are measured with the bottom facet of the device on a heat sink and the remainder open to ambient air at 293 K. A clear plastic tube of 1.57 mm diameter, with a 2 mm long water droplet plug, is connected to the outlet to facilitate observations. The water plug offers a nominal pumping load of about 50 Pa. An input power of 296 mW/cm^2 results in a typical gas flow rate of 6.6×10^{-3} cc/min-cm^2 across a single zeolite disk (zeolite-1, Fig. 2); the temperature gradient measured across the zeolite is typically 15.7 K/mm. (The experimentally determined bulk thermal conductivity of this zeolite is about 0.5 W/m K.)

A similar setup is used to characterize the pressure response at the outlet of the device, except for the fact that the

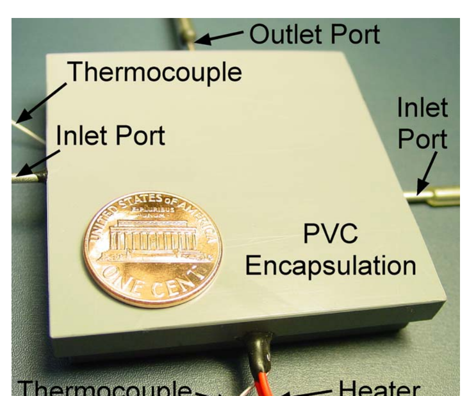

FIG. 3. (Color online) Zeolite-based Knudsen pump with PVC encapsulation. The packaged volume is $55 \times 55 \times 12$ mm^3.

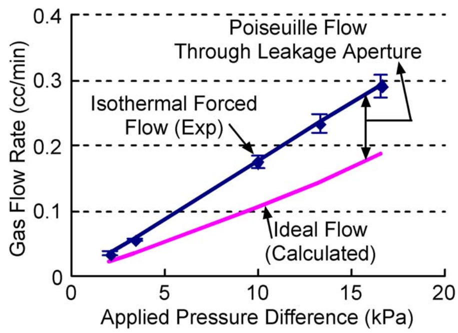

FIG. 4. (Color online) Experimental characterization of pressure-driven gas flow across a typical ≈25 mm diameter and ≈1.15 mm thick zeolite disk.

outlet is sealed in this case. (The volume of the heated chamber, together with the dead volume of the attached tubing, is 2.8 cm^3.) A piezoresistive pressure sensor (Kulite Semiconductor Products Inc., NJ) is used to record the outlet pressure relative to the ambient. Figure 5 shows a typical response (P_{He}), corresponding to the experimentally measured temperature at hot and cold thermocouples, plotted as T_{He} and T_{Ce}, respectively. It also shows the numerically modeled pressure (P_{Hm}), and the fitted estimates for temperatures of the hot and cold facets of the zeolite, T_{Hm} and T_{Cm}, respectively.

Given the earlier characterization of the leakage aperture per unit area in our zeolite samples, we expect that the leakage apertures for a typical zeolite disk of 48 mm diameter are 21.1–27.8 μm in diameter. In comparison, the fitted value of the leak aperture, as determined from the semianalytical simulation model—see Fig. 5, P_{Hm}—is ≈37.5 μm while heating, and ≈31.6 μm while cooling. The difference in the leak apertures during heating and during cooling is potentially due to the hydraulic path followed by gas molecules in these cases. The pressure transient when the pump turns on is adequately captured by the fitted parameter for the thermal time constant of the hot side of the zeolite disk. This time constant is 125% slower than the heating time constant for the heater itself (as denoted by plot T_{Hm} in Fig. 5). When the pump turns off, the heater cools at the same rate as its immediate surroundings. Based on these fitted parameters, the modeled pressure profile, P_{Hm}, reproduces the experimentally observed pressure profile, P_{He}, with a root mean squared error of <0.15 kPa (Fig. 5).

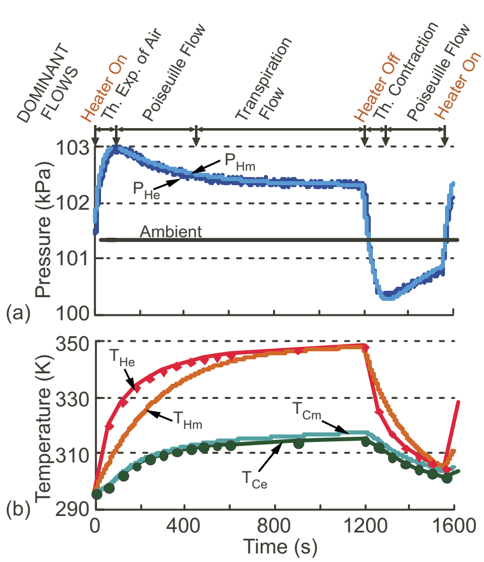

FIG. 5. (Color online) (a) Experimental (P_{He}) and modeled (P_{Hm}) pressure transients recorded with a sealed outlet for a single side of the Knudsen pump, showing a root mean square error of <0.15 kPa. (b) T_{He} and T_{Ce} show the recorded temperature from the thermocouples. The corrected temperatures are T_{Hm} and T_{Cm} respectively.

It is notable that zeolite group members are known to have charge balancing ions of Na, K, Ca, etc., located within the channels that may affect the permeability of certain gasses.[17,18] This aspect of the pump behavior was not studied in our preliminary investigations.

In conclusion, it appears evident that a zeolite-based Knudsen pump using naturally occurring nanoporous clinoptilolite (and potentially other zeolites as well) can be built for atmospheric pressure operation. Having no moving parts, it offers the promise of high reliability. The architecture of the Knudsen pump presented in this letter can be potentially extended to serial or parallel multistage pumping. These configurations can result in gas flow rates of 0.005–0.02 cc/min-cm^2 of zeolite disk, or gas pumping pressure on the order of 50 kPa, for power density levels of roughly 1 W/cm^2. Knudsen pumps have potential applications in gas chromatographs, mass spectrometers, and systems requiring precise control of gas flow.

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[1] K. Arshak, E. Moore, G. M. Lyons, J. Harris, and S. Clifford, Sens. Rev. **24**, 181 (2004).
[2] S. Terry, J. H. Jerman, and J. B. Angell, IEEE Trans. Electron Devices **26**, 1880 (1979).
[3] E. T. Zellers, S. Reidy, R. A. Veeneman, R. Gordenkar, W. H. Steinecker, G. R. Lambertus, H. Kim, J. A. Potkay, M. P. Rowe, Z. Qiongyan, C. Avery, H. K. L. Chan, R. D. Sacks, K. Najafi, and K. D. Wise, IEEE International Conference on Solid State Sensors, Actuators and Microsystems (Transducers), 2007 p. 1491.
[4] D. J. Laser and L. G. Santiago, J. Micromech. Microeng. **14**, R35 (2004).
[5] H. Kim, A. A. Astle, K. Najafi, L. P. Bernal, and P. Washabaugh, IEEE International Conference on Micro Electro Mechanical Systems (MEMS), 2007 p. 127.
[6] F. Li, Y. Jiang, L. Yu, Z. Yang, T. Hou, and S. Sun, Appl. Surf. Sci. **252**, 1410 (2005).
[7] E. H. Kennard, *Kinetic Theory of Gases* (McGraw Hill, New York, 1938), p. 327.
[8] O. Reynolds, Philos. Trans. R. Soc. London **170**, 727 (1878).
[9] J. C. Maxwell, Philos. Trans. R. Soc. London **170**, 231 (1879).
[10] M. Knudsen, Ann. Phys. **31**, 205 (1910).
[11] S. E. Vargo and E. P. Muntz, Rarefied Gas Dynamics: 22nd International Symposium, 2001 p. 502.
[12] S. McNamara and Y. B. Gianchandani, J. Microelectromech. Syst. **14**, 741 (2005).
[13] G. E. Karniadakis, A. Beskok, and N. Aluru, *Microflows and Nanoflows: Fundamentals and Simulation* (Springer, New York, 2005), p. 17.
[14] L. B. Loeb, *The Kinetic Theory of Gases* (McGraw Hill, New York, 1934), p. 355.
[15] F. Sharipov, J. Vac. Sci. Technol. A **15**, 2434 (1997).
[16] N. K. Gupta and Y. B. Gianchandani, IEEE International Conference on Solid State Sensors, Actuators and Microsystems (Transducers), 2007, p. 2329.
[17] J. M. Kalogeras and A. Vassilikou-Dova, Cryst. Res. Technol. **31**, 693 (1996).
[18] U. Simon and M. E. Franke, Microporous Mesoporous Mater. **41**, 1 (2000).
[19] N. K. Gupta and Y. B. Gianchandani, IEEE International Conference on Micro Electro Mechanical Systems (MEMS), 2008 p. 38.