We study the effect of a gradient of solvent quality on the coil-globule transition for a polymer in a narrow pore. A simple self-attracting self-avoiding walk model of a polymer in solution shows that the variation in the strength of interaction across the pore leads the system to go from one regime (good solvent) to the other (poor solvent) across the channel. This may be thought analogous to thermophoresis, where the polymer goes from the hot region to the cold region under the temperature gradient. The behavior of short chains is studied using exact enumeration whilst the behavior of long chains is studied using transfer matrix techniques. The distribution of the monomer density across the layer suggests that a gate-like effect can be created, with potential applications as a sensor.

In the last few years, much attention has been paid to studying the confinement of polymer chains [1–6]. A confined polymer chain exhibits specific and interesting properties, which have potential applications in diverse fields such as steric stabilization of colloidal dispersions, behavior of thin films, the adsorption behavior of polymers/gels, use as surface coatings, understanding the behavior of polymers in nanopores etc [1]. However, in most of these studies, the surface has been taken as either neutral or adsorbing and statistical mechanics concepts have been applied to the derivation of equilibrium properties.

When the confining surfaces are put at different temperatures (Fig. 1 a), many interesting phenomena take place such as the separation of macromolecules in organic solvents [7], and thermally driven crowding of nucleotides, considered as a possible mechanism in the molecular evolution of life [8, 9]. Microfluidic applications include colloidal accumulation [10]. The temperature gradient acts like an external field, which can drive the system to the steady state, where local thermal equilibrium exists, and local thermodynamic quantities can be defined. The conductivity, diffusion, and viscosity are just some of the physical properties of such a system which have been studied extensively in the past years. These systems are important for the understanding of biological processes such as those involved in inflammation, wound healing and cancer metastasis, etc [11]. In these phenomena, biomolecules move under the chemical gradient. The manipulation of a temperature or other gradient is useful in many applications which require the control of flow at the nano-metric scale, ranging from the control of drug delivery by changing physiological parameters in the tissue, to the control of flow to a nano-metric sensor, where the gradient plays an important role [12].

The presence of a polymer in the temperature gradient is then used as a gating device, which depending on the gradient will either open or close the pore.

There have been a number of studies, experimental, numerical and theoretical, on the behavior of polymer brushes grafted to the walls of nano-metric channels, and their response to changes in solvent quality [13–15], electric field [16], temperature etc [10, 12, 17].

As the temperature is lowered, a single polymer chain in solution undergoes a transition from the coil (high temperature) state to the globule (low temperature) state [1]. Equilibrium properties of the coil-globule transition are usually derived from the partition function, which is the sum over Boltzmann weighted ($e^{\beta \epsilon}$) energy conformations [18, 19]. It is also possible to study the coil-globule transition by changing the solvent quality or attractive interaction ($\epsilon > 0$) among monomers. The solvent is called a good solvent if polymer is found to be in the coil state, whereas it is referred as a poor solvent if polymer is in the globule state [1]. It is not possible to obtain the
equilibrium properties of a single polymer chain confined between two walls at different temperature, but it is possible to examine the behavior of a polymer chain to a gradient of solvent quality across a narrow two-dimensional channel. This solvent quality gradient may be thought of as resulting from a salt gradient or a temperature gradient (although as discussed above the system is not strictly in equilibrium, but in the steady state). Such a gradient could arise as a result of a difference in the affinity the salt has with the top and bottom surfaces of the channel for the salt, or in the case of an ionic salt, one could imagine an electric field giving rise to a gradient in the salt concentration.

In this report we present the behavior of short and long polymers under such a solvent gradient. The short polymer case is studied using the exact enumeration method, whilst the long polymer case uses the transfer matrix method. We start by presenting the basic model and methods used. We then present the results for both short and long chains as a function of the solvent gradient. Since we are interested in equilibrium (or pseudo-equilibrium) properties of the polymer, we will work with an implicit solvent. This is valid assuming that the solvent quality gradient affects the (effective) nearest-neighbor interaction, and not the chemical potential of the monomers. This is the choice often chosen for solvent-quality driven translocation (see for example Refs. 20, 21) and is reasonable if one thinks of the monomer-monomer interactions having an electro-static component, where the salt concentration changes the screening length, for example. As long as the screening length is not too large, the approximation of keeping only nearest-neighbor interactions is reasonable [22]. In the case of the temperature gradient, the change of temperature will directly affect the Boltzmann weight associated with the nearest-neighbor interaction.

The aim of this paper is to obtain the distribution of density across the channel width as a function of the solvent gradient $\Delta \epsilon$. The paper ends with a brief discussion on its application as a gate for use as a sensor.

The model used here consists of a self-avoiding random walk on the square lattice with nearest-neighbor (nn) interactions representing the difference in the affinities between the monomers and between monomers and the solvent/salt molecules [18]. In the spirit of such coarse-grained models, the step length, which is the same as the lattice spacing in this case, corresponds to a statistical monomer, made up of a number of real monomers.

The thermodynamic properties of a polymer in a solvent of uniform quality are contained in the averages of physically relevant quantities calculated in the canonical or grand canonical ensembles, hence requiring the calculation of the corresponding partition functions. The canonical partition function for the homogeneous polymer of length $N$ may be written

$$Z_N = \sum_{\text{walks}} \tau^{N_I}$$

where the sum is over self-avoiding walks, $\tau = \exp(\beta \epsilon)$ and $N_I$ are the Boltzmann weight for the non-bonded nearest-neighbor interaction and the number of nearest-neighbor contacts, respectively. The nearest-neighbor interaction is attractive, so $\tau > 1$. We have chosen a sign convention such that the interaction strength $\epsilon > 0$.

The quality of the solvent is changed by varying either the temperature or the interaction strength $\epsilon$. For the two-dimensional square lattice model, the $\theta$ temperature, corresponding to the collapse transition of the polymer, for the homogeneous model has been found to be at $\beta \epsilon = 0.658 \pm 0.005$ [18]. For $\beta \epsilon$ greater than this value, the polymer is in the bad solvent, whilst for a value lower than this, the polymer is in the good solvent.

The solvent quality is now allowed to vary with the distance $y$ from the lower wall, and so the interaction strength will be a function of $y$, $\epsilon(y)$. At the zeroth layer the nn interaction is zero, whereas at the $L^{th}$ layer, it is $\epsilon$. We define the gradient interaction $\Delta \epsilon = \epsilon/(L - 1)$, such that the interaction is given by $\epsilon(y) = y \Delta \epsilon$ for layer $y$.

To encode this variation in our model, it is necessary to consider the weights differently in the $x$ and $y$ directions, $\tau_x(y)$ and $\tau_y(y)$. The solvent quality is uniform in the $x$ direction, and so

$$\tau_x(y) = \exp(\beta \epsilon(y)) \quad (2)$$

On the other hand the interaction varies in the $y$ direction, and so we choose to define the Boltzmann weight in the $y$ direction with the average interaction strength between the two layers involved, such that a nn interaction between layers $y$ and $y + 1$ will be written as

$$\tau_y(y) = \exp\left(\frac{\beta}{2} [\epsilon(y) + \epsilon(y + 1)]\right) \quad (3)$$

We study two limiting cases, the case of the short chain and the case of the very long chain. In both cases we take the width of the channel to be $L = 9$ lattice spaces.
The short chain case was studied using exact enumeration techniques, where all configurations of a chain of length $N = 30$ are enumerated, taking into account the $y$ coordinate of any interaction and differentiating between interactions in the $x$ and $y$ direction. In practice this was done by fixing one end of the chain in one of the layers, enumerating all the configurations and then averaging the results over all possible initial layer choices. In this case the canonical partition function (Eq. 1) for the strip can be written as

$$Z_N^L = \sum_{L,N_1} C(N_1, L) \exp(\beta \varepsilon(y) N_1), \quad (4)$$

The average number of monomers in each layer ($\langle n(y) \rangle$) can be calculated as

$$\langle n(y) \rangle = \frac{\sum_{L,N_1} n(y) C(N_1, L) \exp(\beta \varepsilon(y) N_1)}{Z_N^L}. \quad (5)$$

Since in the case of exact enumeration, the number of conformations increases $\mu^N N^\gamma - 1$, where $\mu$ and $\gamma$ are the effective coordination number of the lattice and exponent respectively $[15]$ and hence it is not possible to go for a longer chain. However, it is possible to use transfer matrix techniques to get long chain behavior. In this case, it is more convenient to work in the grand-canonical ensemble, defining the grand-canonical partition function by

$$Z = \sum_N K^N Z_N, \quad (6)$$

where $K$ is the fugacity, which controls the average length of the polymer through:

$$\langle N \rangle = \frac{K}{Z} \frac{\partial Z}{\partial K}. \quad (7)$$

Note that in this context $K$ does not relate to a chemical potential in the usual way, since the polymer is not allowed to exchange monomers with a reservoir of monomers.

The partition function may be calculated exactly on a strip of length $L_x \to \infty$ by defining a transfer matrix $\mathcal{T}$. If periodic boundary conditions are assumed in the $x$-direction, the partition function for the strip is given by:

$$Z_L = \lim_{L_x \to \infty} \text{Tr} \left( \mathcal{T}^{L_x} \right). \quad (8)$$

The average number of monomers in each layer ($\langle n(y) \rangle$) can be calculated as

$$\langle n(y) \rangle = \frac{\sum_{L,N_1} n(y) C(N_1, L) \exp(\beta \varepsilon(y) N_1)}{Z_N^L}. \quad (5)$$

FIG. 3. (Color online) Distribution of monomers as a function of interaction gradient ($\beta \Delta \varepsilon$) for different layers: (a) Using Exact enumeration (short chain); (b) Using Transfer matrix (long chain).

where $\lambda_0$ is the largest eigenvalue of the transfer matrix.

The fugacity $K$ was chosen such that the average length of the polymer was taken to infinity setting $\lambda_0(K) = 1$.

In Fig. 3(a), we have plotted the distribution of average number of monomers in each layer obtained from exact enumeration as function of $\beta \Delta \varepsilon$, whereas in Fig. 3(b) we showed the density distribution in each layer as a function of $\beta \Delta \varepsilon$ for transfer matrix case. It is evident from these plots that at zero interaction gradient, the monomer density is maximum in the middle layer and decreases, when
one moves towards the surface. In order to have the compact structure (collapsed state) the average number of contacts needs to be maximized. This can be achieved only if monomers are distributed (in a compact way) near the poor solvent side ($L \approx 8$). In present case (chain size $N = 30$ (31 monomers)), the four layers near $L = 8$ (poor solvent side) are populated and, thus the average number of monomers in each layer is nearly 8, which give rise collapsed state. It may be noted that the surface here is the hard wall. When $\Delta \epsilon$ increases, the monomer density shows a clear shift towards layer eight, where nearest neighbor interaction is maximum (poor solvent). This is analogous to thermophoresis, where the monomer moves away from the hot surface to the cold surface [10]. The finite size effect one may notice from Fig. 3a and 3b, where average number of monomers in layer 4 decreases to zero, whereas for a longer chain it approaches towards the maximum so that it can have a compact structure.

In figures 4 and 5 we show the results for the distribution of monomers as a function of the layer and interaction gradient. The color corresponds to the density. For the short chain, we plot the average number of monomers in each layer as a function of $\beta \Delta \epsilon$, whilst in the long chain case we plot the density of monomers per layer. In each case, the qualitative features are the same: for a good solvent (or at high temperatures) the polymer is uniformly distributed across the width of the strip, hindering the passage down the strip, whilst at low temperatures, the polymer collapses into the region (yellow shaded) where the solvent quality is poor, liberating the good solvent portion of the strip i.e. opening up the lower part of the strip.

It has been observed that walls coated with polymer brushes act as a valve in a nanocapillary tube [24] under a pressure gradient. Here our studies revealed that it is possible to design a valve, which can act as a solvent sensor or temperature sensor. In order to implement it, let us consider a capillary tube grafted with many polymers on its surface as shown in Fig. 6. Let us assume the surface of a tube is at low temperature or tube is filled with a poor solvent. In such a case, the polymer will be in the collapsed state and flow of liquid is possible through pore (Fig.6a). When a good solvent comes inside the capillary tube or the temperature of the surface changes [10], there will be a solvent gradient [15] or temperature gradient [10], which will swell the polymer and thereby stops the flow of liquid. By suitably adjusting the gradient and temperature, it is then possible to gate the pore/capillary by changing one or other parameters. Whilst in a narrow pore there is no sharp transition from the swollen (good solution) to collapsed (poor solution) behavior, we can derive an estimate of where the pore gating will occur by identifying the peak of the density fluctuations as a function of the temperature. This is shown as a phase diagram [25] for the short polymers in figure 4. The “transition” line lies on the curve $\beta \Delta \epsilon = 0.118(1)$, indicating as expected, that the two parameters are interchangeable. For the long polymers we find $\beta \Delta \epsilon = 0.140(1)$

Using the lattice model of polymers along with an
exact enumeration technique and the transfer matrix method, we obtained the exact density distribution of monomers across the strip as a function of the gradient of solvent quality. We have analyzed the chain of different lengths (finite chain length) and found that the qualitative behavior remains same and similar to a longer chain obtained through transfer matrix calculations. This is analogous to the distribution of monomers across the strip put at two different temperatures, where the usual concepts of equilibrium statistical mechanics fail. By changing $\beta \Delta \epsilon$, it was shown that gating of the pore may be created by either changing solvent quality gradient at fixed temperature or equivalently changing the temperature at a fixed (non-zero) gradient. Since one could imagine controlling the solvent quality by applying an external field, we proposed a strategy for gating a nanopore. The model presented here is simple, but provides the underlying mechanism involved in such sensors.

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