Monte Carlo simulation of polymer adsorption

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Abstract We developed and employed the incremental
gauge cell method to calculate the chemical potential (and
thus free energies) of long, flexible homopolymer chains of
Lennard-Jones beads with harmonic bonds. The free energy
of these chains was calculated with respect to three exter-
nal conditions: in the zero-density bulk limit, confined in a
spherical pore with hard walls, and confined in a spherical
pore with attractive pores, the latter case being an analog
of adsorption. Using the incremental gauge cell method, we
calculated the incremental chemical potential of free poly-
mer chains before and after the globual-random coil transi-
tions. We also found that chains confined in attractive pores
exhibit behaviors typical of low temperature physisorption
isotherms, such as layering followed by capillary condensa-
tion.

Keywords Monte Carlo · Chemical potential · Flexible
chains · Lennard-Jones · Gauge cell · Polymers

1 Introduction

The ability to calculate the free energy of confined chain
molecules is one of the key issues in modeling various
processes that involve polymer adsorption, including poly-
mer chromatography, membrane separation, petrochemical
processing, and more. In molecular simulations, free en-
ergies are typically obtained via thermodynamic integra-
tion along a continuous path of equilibrium states connect-
ing the system of interest to a system where the free en-
ergy is known, or using various techniques for obtaining

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the chemical potential in the system of interest that typi-
cally require *insertions* (or, in some cases, removals) of new
molecules into the system, tracing back to the Widom parti-
cle insertion technique and the grand canonical MC method
(Widom 1963; Norman and Filinov 1969). The efficiency
of all insertion-based techniques diminishes swiftly as the
density and the molecule size increase, due a high probabil-
ity of inserted particles overlapping with exisiting ones. For
polymer molecules, this problem is aggravated dramatically
as the polymer length increases, and the confinement of the
molecule within pores makes insertions even more difficult.

Two general approaches to solving these problems have
been developed. The first approach is based on "growing"
the trial molecules into available (low energy) space with
a configurational bias (Rosenbluth and Rosenbluth 1955;
Frenkel et al. 1991; de Pablo et al. 1992); this is the so-called
Rosenbluth insertion. This approach suffers from two draw-
backs: first, as the fluid becomes denser, only short chains
can "find" low energy configurations, and second, the trial
chains are not generated according to a Boltzman distribu-
tion (Frenkel and Smit 2002). Obviously, the former prob-
lem is aggravated rapidly as the density and chain length
increase. Thus, the longer the chain is, the less dense the
surrounding fluid should be to obtain statistically relevant
results.

An alternative method of calculating the chemical po-
tential of chain molecules was purposed by Kumar et al.
(1991), termed the modified particle insertion method. The
disadvantages of configurationally bias insertions are over-
come by calculating the *incremental chemical potential*, that
is, the difference in chemical potentials between the chains
of $n + 1$ and n monomers. In practice, this is done using
trial additions (and/or removals) of a monomer at an end
of an equilibrated polymer chain. One obvious disadvan-
tage is the necessity to perform n independent simulations

to rigorously determine the chemical potential for one *n*-mer chain. However, several studies (Grassberger and Hegger 1995; Spyriouni et al. 1997) have shown that the incremental chemical potential is independent of chain length for systems over the theta temperature, which corresponds to the conditions at which the entropic contributions outweigh the attraction between the monomers, and the chain behaves as a random coil. If solvent composition changes rather than the temperature, the solvent where the polymer behaves as a coil is referred to as a "good solvent". Thus, for a complete (if approximate) description of coil-like (good solvent) polymers, several short-chain length simulations are performed, and one long chain length, limiting-case simulation can be used to extrapolate the remaining points. The increment method has apparent advantages over the Rosenbluth technique (where the entire chain has to be inserted at once, even if the available space for each monomer is searched for in advance) for long polymers and dense systems, although the problem of low efficiency of insertions/removals in dense systems still exists.

The gauge cell Monte Carlo method (Neimark and Vishnyakov 2000, 2005) is a MC technique used to efficiently calculate phase equilibria and transitions, especially in dense and/or heterogeneous systems. The simulation system is constructed as follows: a system of interest, or sample cell, is placed in chemical equilibrium with a reference, or gauge cell of limited capacity. This mesoscopic canonical ensemble, or mesocanonical ensemble, is an intermediate between the canonical ensemble and the grand canonical ensemble. The gauge cell brings about two advantages: it serves as a meter of chemical potential, and its limited volume restricts density fluctuations in the sample cell. For confined dense systems of small molecules, the gauge cell method was proven more efficient than the Widom insertion (Neimark and Vishnyakov 2005). In this work, we have extended the gauge cell method to calculate the incremental chemical potential of chain molecules.

2 Model

A simulation using the incremental gauge cell method is constructed as follows: a 'system' cell (that is, the system of interest, whether it is a periodic box or a confinement with an external potential) is placed in contact with a gauge cell. The system cell contains a *chain* of *n* monomers, while the gauge contains a *fluid* of n_g monomers. Note that in this work we consider the properties of a single polymeric molecule in confinement as compared to that in the corresponding diluted bulk solution. The total number of monomers, $n_t = n + n_g$, is fixed, as are the volumes of both cells and the temperature. Monomers are allowed to move from either end of the chain into the gauge, and vice versa. As constructed, the total system (system cell + gauge cell) can be

considered a canonical ensemble, as n_t, V, and T are constant. Thermodynamically, this scheme will correspond to the minimization of the total Helmholtz free energy represented as the sum of the free energy of the *n*-mer in the system cell and the free energy of n_g monomers in the gauge cell,

$$F_t(n_t, V, V_g, T) = F(n, V, T) + F_g(n_g, V_g, T) \quad \Rightarrow \quad \min \tag{1}$$

where V and V_g are the system cell and gauge cell volumes. The incremental chemical potential is defined as the difference of chemical potential between an $(n+1)$-mer chain and an *n*-mer chain. As first formulated by Widom (1963), this can be approximated as a finite difference in Helmholtz free energies,

$$\mu_{\text{incr}}(n) = F(n + 1, V, T) - F(n, V, T). \tag{2}$$

Knowing that $F = -k_B T \ln[Q(n, V, T)]$, where $Q(n, V, T)$ is the canonical partition function, we see that μ_{incr} is a ratio of partition functions; $\mu_{\text{incr}} = -k_B T \ln[Q(n + 1, V, T)/Q(n, V, T)]$. Plugging in the partition function and canceling terms, we arrive at an expression similar to Widom's particle insertion method:

$$\mu_{\text{incr}}(n)$$
$$= -k_B T \ln\left[\frac{1}{\Lambda^3} \int_{V_{\text{seg}}} d\mathbf{r}_{\text{seg}} \langle \exp(\phi_{\text{seg}}(\mathbf{r}_{\text{seg}}; \mathbf{r}^n)) \rangle_{n, V, T} \right], \tag{3}$$

where Λ is the de Broglie wavelength, $\mathbf{r}_{\text{seg}}$ refers to the position an additional trial segment inserted onto the end of the chain, and ϕ_{seg} is the potential energy of $\mathbf{r}_{\text{seg}}$ interacting with the system, $\mathbf{r}^n$. Equation (3) is the basis of the Kumar et al. (1991) modified particle insertion method. Similar to the Widom scheme, a "trial monomer" is added to the chain undergoing a standard canonical ensemble simulation, and trial insertions do not influence the configuration of the system. Because the "trial monomer" is bonded to the monomer terminating the chain, it is inserted only into a small volume V_{seg} around the chain end, since for all other configurations the energy of the bond is extremely high and the contributions to the average in (3) are insignificant.

In the incremental gauge cell method, the monomer at the end of the chain contained in the system cell is allowed to exchange with a fluid of monomers in the gauge cell. The probability to observe a configuration with an *n*-mer chain in the system cell and n_g monomers in the gauge cell is proportional to

$$P_n = P_{n_g} \propto \exp\left\{ -\frac{1}{k_B T} [F(n, V, T) + F_g(n_g, V_g, T)] \right\} \tag{4}$$

and, correspondingly,

$$P_{n+1} = P_{n_g-1} \propto \exp\left\{-\frac{1}{k_B T}[F(n+1, V, T) \right.$$
$$\left. + F_g(n_g - 1, V_g, T)]\right\}. \quad (5)$$

Taking the ratio of (4) and (5), and utilizing the definition of μ_{incr} from (2), we obtain

$$\frac{P_{n+1}}{P_n} = \frac{P_{n_g-1}}{P_{n_g+1}} = \exp\left\{-\frac{1}{k_B T}[\mu_{incr}(n) + \mu_g(n_g - 1)]\right\}, \quad (6)$$

and

$$\mu_{incr}(n) = \mu_g(n_g - 1) + k_B T \ln(P_{n_g}/P_{n_g-1}). \quad (7)$$

Equation (7) is the main equation of the gauge cell method. It relates the chemical potential of the monomer fluid in the gauge cell to the incremental chemical potential of the chain in the system cell. If the equation of state of the reference fluid located in the gauge cell is known, μ_{incr} is determined from the histogram of the number of particles in the gauge P_{n_g} obtained in the course of gauge cell MC simulations. Up to this point, we have not made any assumptions regarding the gauge cell fluid. The most convenient and logically sound choice is to treat it as an ideal gas. If we then substitute the expression for the chemical potential of an ideal gas into (7), we finally obtain

$$\mu_{incr}(n) = -k_B T \ln\left(\frac{V_g}{\Lambda^3 n_g}\right) + k_B T \ln(P_{n_g}/P_{n_g-1}). \quad (8)$$

This and (7) are the final expressions of the ideal gas gauge cell method (Neimark and Vishnyakov 2005). Note that when the distribution of particles in the gauge cell is sufficiently wide, the second term on the right hand side of (7) and (8) is negligible. Then, $\mu_{incr}(\bar{n}) = \mu_g(\bar{n}_g)$; this is called mean density gauge cell.

In this work, the chain in the system cell is equilibrated via traditional MC moves. These include bonded-monomer displacement, reptation, crankshaft (Verdier and Stockmayer 1962), and configurational bias regrow (Siepmann and Frenkel 1992). Note that this regrow move differs from the Rosenbluth insertions described above; here, a regrow move consists of selecting a random bond, removing the chain from that bond to the terminal monomer, and then attempting to regrow a new chain via configurational bias. The regrow is then accepted or rejected in a way that negates the initial bias. In addition to these canonical ensemble equilibration moves for the polymer chain in the system cell, an exchange moves are implemented to sample "chemical equilibrium" between the system and gauge cells. These include

attempted insertion of a monomer from the gauge into the system cell with its attachment to the end of the chain accepted with the probability of

$$p_{ins} = \min\left\{1, \exp\left(-\Delta\phi_{ins}/k_B T - \ln\left[\frac{V_g}{n_g V_{seg}}\right]\right)\right\}, \quad (9)$$

and attempted detachment of the bead from the polymer chain end with its removal from the system and insertion into the gauge:

$$p_{rem} = \min\left\{1, \exp\left(-\Delta\phi_{rem}/k_B T - \ln\left[\frac{(n_g + 1)V_{seg}}{V_g}\right]\right)\right\}, \quad (10)$$

where $\Delta\phi_{ins}$ and $\Delta\phi_{rem}$ are the energies of inserting or removing a monomer to/from the end of the chain, respectively. These expressions are similar to the standard gauge cell acceptance probabilities (Neimark and Vishnyakov 2000, 2005), except for two features: first, V in the original equations is replaced here by V_{seg}. This is because the monomers from the gauge are only inserted at the end of the chain, into the volume V_{seg}, and not into the entire system volume V. Second, the number of molecules in the system cell N in the log term from the original equations is omitted; this is because we always have just one chain in the system cell and thus, $N = 1$.

The chain is modeled as a flexible "necklace" of bonded Lennard-Jones (LJ) beads. The LJ potential was truncated at $r_c = 10\sigma$, and acts on all non-bonded monomers. The bonds are modeled as harmonic-springs,

$$U_{bond}(r) = \frac{1}{2}\kappa_b(r - r_0)^2 \quad \text{for } 0.5 \leq r \leq 1.5$$
$$= \infty, \quad \text{otherwise.} \quad (11)$$

For this study, we set $\kappa_b = 400\varepsilon/\sigma^2$, and the equilibrium bond length $r_0 = 1\sigma$. The volume of action of the harmonic potential (11) is set as V_{seg}. No restrictions are placed on bond angles or dihedrals; the chain is fully flexible. We consider two situations: a "free" chain in the zero-density limit (simulations performed with no boundary conditions) and polymers confined to the spherical pore of 7.5σ in diameter. Monomer interaction with the pore wall are modeled with both the hard wall potential, where $U_{ext}(r) = 0$ for $r < R$, and $U_{ext}(r) = \infty$ for $r > R$, and with the spherically integrated, LJ potential (Ravikovitch and Neimark 2002). To compare these two confinements, pores are sized so that the volume accessible to monomers is equal. For the hard wall pores, $d_{acc} = 2R + \sigma$, and for the adsorbing pore, $d_{acc} = 2R - 2r_w(U_{ext} = 0) + \sigma$, where $r_w(U_{ext} = 0)$ is the distance from wall where the external potential is zero. In this study, we selected $d_{acc} = 7.5\sigma$. For pores of this size, at $\rho\sigma^3 = n\sigma^3/V_{acc} = 1$, the chain lengths are approximately 220 monomers long, where $V_{acc} = 4\pi/3(d_{acc}/2)^3$.
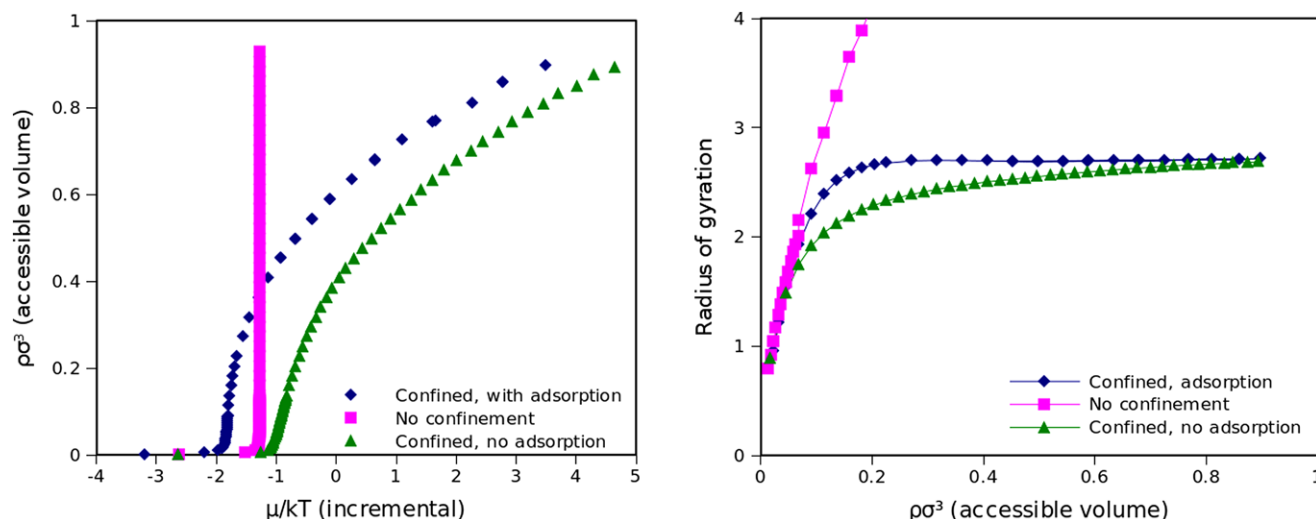
Fig. 1 *Left*: The incremental chemical potential, μ_{incr}, calculated as a function of chain length for an unconfined chain, chain confined in a hard-wall pore and confinement in a pore with an attractive adsorption potential at $T^* = 8$. *Right*: The radius of gyration for the same systems

3 Results

To observe the balance of entropic and enthalpic effects, we varied the temperature from $T^* = 1$ to $T^* = 8$. For single free chains, it is well known that below the Θ-temperature, monomer-monomer interactions dominate and the chain collapses into a condensed form called a globule. Similarly, we know that above this temperature, thermal motion dominates and the chain behaves as a random coil (Flory 1953). The theta temperature of the flexible LJ chains is between $T^* = 3$ and 4, depending the potential cut-off radius (Grassberger and Hegger 1995; Graessley et al. 1999) and chain length. Therefore, we selected cases below ($T^* = 1$), near ($T^* = 2$), in ($T^* = 3.2$), and above ($T^* = 8$) the Θ-temperature. To compare the structure of each system, we calculate the radius of gyration, R_G:

$$R_G^2 = \sum_i^n (\mathbf{r}_i - \mathbf{r}_{cm})^2 / n. \tag{12}$$

All values of R_G discussed are reduced by σ. To compare chains from all systems, the figures below plot all curves in terms of monomer density, that is, $\rho\sigma^3 = n\sigma^3 / V_{acc}$, including the free chain, which is actually calculated in the limit of zero density. However, because they are all reduced by the same volume, chain length effects are numerically comparable.

The incremental chemical potential for all three systems (unconfined chain, chain confined in a pore with hard walls and the chain confined in a pore with "adsorbing" attractive walls) at $T^* = 8$ is presented in Fig. 1a, and their corresponding radius of gyration in Fig. 1b. As predicted, μ_{incr} of a free chain (no confinement) does not depend on the chain length once the limiting chain length is reached

($n \sim 5$). Once the chain is confined, it encounters an immediate entropic penalty imposed by the limitations of possible polymer conformations by pore walls. While the incremental chemical potential of unconfined chains has no dependence on chain length, it becomes a strong function of the pore filling when the chain is confined. The incremental chemical potential increases monotonically with the chain length. The inclusion of an attractive adsorption potential does not significantly alter the behavior of the curve, suggesting that the entropic effects at such a temperature outweigh both the internal and external attractive forces. The relatively constant shift between the confined hard wall and confined adsorbing walls is indicative of the strength of adsorption potential. The structure of the free chain is that of a random, self-avoiding coil. We found that for the free chain, $R_G \propto (n-1)^{0.590}$ (tested up to $n = 500$). This scaling exponent is very close the most accurate literature result of 0.5877 by Li et al. (1995), further validating the algorithm. The R_G of the chain confined in the non-adsorbing hard-wall pore show that only for very short chains ($n < 15$) confinement does not impact the R_G of the polymer. After that, R_G approaches a value representative of the filled pore. When the adsorption potential is present, R_G reaches a plateau quickly ($n \sim 50$). This indicates that the chain is evenly distributed in the pore volume, and an increase in the number of monomers does not change the distribution of mass in the pore significantly. Essentially, this is to the adsorption of a super-critical fluid.

The next temperature, $T^* = 3.2$, is close to the Θ-temperature calculated by Graessley et al. (1999) using a cut-off radius of 2.5 and a shifted potential, which was $T^* = 3.18$. Our results for this system are displayed in Fig. 2. The incremental chemical potential of the free chain and hard-wall confined chain are qualitatively similar to the higher
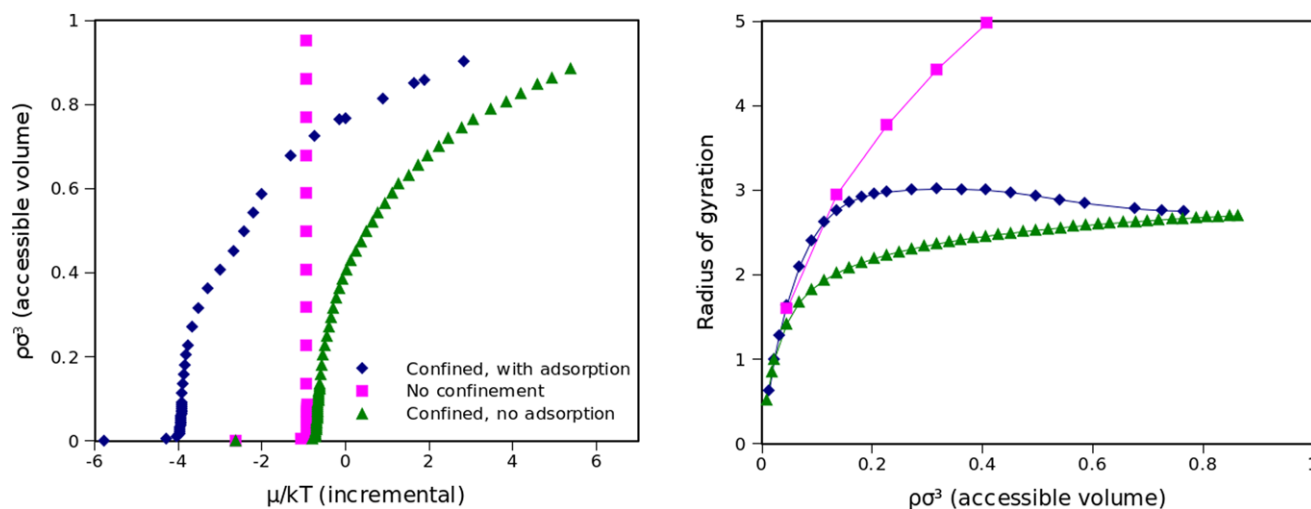
Fig. 2 *Left*: The incremental chemical potential μ_{incr} calculated as a function of chain length for an unconfined chain, chain confined in a hard-wall pore and confinement in a pore with an attractive adsorption potential at $T^* = 3.2$. *Right*: The radius of gyration for the same systems
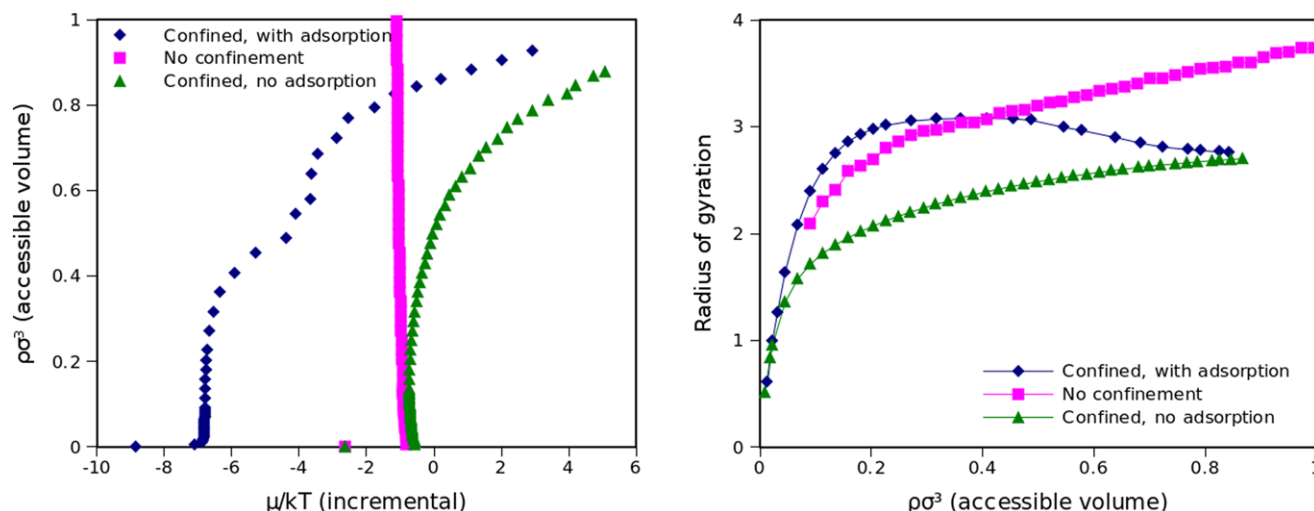

Fig. 3 *Left*: The incremental chemical potential μ_{incr} calculated as a function of chain length for a chain in no confinement, confinement with hard-wall repulsion and confinement with an attractive adsorption potential at $T^* = 2$. *Right*: The radius of gyration for the same systems

temperature case. The radius of gyrations are quite similar to that at $T^* = 8$, with the free chain following a power scaling and the confined case following a logarithm-type scaling. This suggests that the entropic contribution still dominates polymer behavior. However, with the inclusion of the adsorptive force, two interesting effects can be observed. First, the incremental chemical potential is no longer a smooth exponential curve like the hard-walled confined chain, but has a weak inflection around a monomer density of 0.4. Second, the R_G of the confined with adsorption chain now has a maximum, as opposed to the high temperature system's R_G with a plateau. The maximum indicates that there is a tendency (albeit a slight one) for the chains to exist closer to the periphery of the pore. While no distinct layering is observed, this tells us that the average density of monomers is higher closer to the adsorbing wall.

Below the Θ-temperature, we have calculated two systems at $T^* = 2$ and 1. The former is closer to the transition point. Figure 3 shows the results for $T^* = 2$. The free chain incremental chemical potential is now clearly depends on chain length. This dependence is logarithmic in nature, and results from the net attractive potential of the growing globule in space. When the chain is placed in the hard-walled pore, confinement effects are first observed for chains ∼50 monomers long. After this point, the incremental potential increases quickly as in the previous cases. The R_G of free and confined chains is now comparable, as they both exhibit a logarithm characteristic when the size of the polymer globule is substantially less than the pore size, but the free chain exhibits a larger R_G (the free chain is about 3 times larger at $n = 200$). However, the adsorbing chain now begins to show distinct regions in incremental chemical potential as a
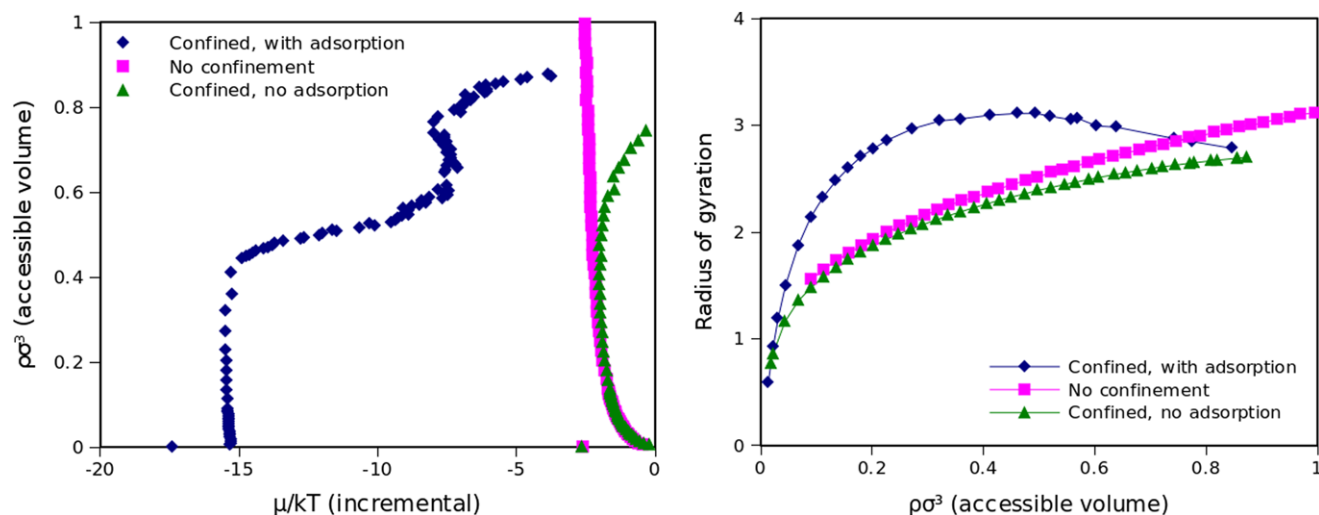
Fig. 4 *Left*: The incremental chemical potential μ_{incr} calculated as a function of chain length for a chain in no confinement, confinement with hard-wall repulsion and confinement with an attractive adsorption potential at at $T^* = 1$. *Right*: The radius of gyration for the same systems

function of the chain length. First, at low densities, a monolayer forms on the pore wall, and μ_{incr} is relatively constant. This is also observed as a clear maximum of R_G with respect to chain length, reflecting the tendency of the mass in the system to be located near the attractive pore wall. As the chain length grows, it must fill the available volume of the pore, and R_G decreases and approaches the value of the hard-wall confined polymer. Second, after the monolayer is formed, another transition is observed as the chain fills the pore. Once the pore is filled, adding additional monomers has a large energetic penalty, and the incremental chemical potential again increases rapidly. The shape of the incremental chemical potential curve is similar to an isotherm of an adsorbing fluid.

The final case studied in this work is well below the Θ-temperature, where the bulk chain behaves as a tightly condensed globule. The results for this case ($T^* = 1$) are presented in Fig. 4. The confinement penalty for such a condensed chain is low—both the incremental chemical potential and the R_G of the chain confined to a hard-walled pore and the free chain are very similar up to moderate lengths of $n \sim 100$. Even for long chains, when the pore is nearly filled at $n = 190$ ($\rho\sigma^3 = 0.86$), the R_G of the confined pore is only fractionally smaller than an unconfined pore (2.7 and 3.0, respectively). As before, when the confined chain is subjected to an adsorption potential, a peak in the R_G is observed, relating to the formation of a monolayer of monomers on the pore wall. A regime of nearly constant μ_{incr} is again observed from $n = 2$ to ~ 80. Unlike the previous case, the transition to a filled pore appears to have a sigmoidal shape reminiscent of a van der Waals loop in a canonical isotherm. The physical phenomenon associated with this characteristic is capillary condensation. As with physisorption of molecular fluids, the lower branch is a layered fluid adsorbed onto

the pore wall (having zero density at the center of the pore), and the upper branch has a nonzero density from the pore center to the pore wall. It's important to remember that we consider just one molecule in these systems, and what's interesting is that many of the same physical insights from adsorption isotherms (μ vs N) are present in these single chain systems (chain length n vs μ_{incr}).

4 Conclusions

We have developed and applied the incremental gauge cell to study adsorption of long, flexible chains in spherical pores with repulsion only and LJ-type potential, as well as free chains with no confinement. Previous work has suggested that the incremental chemical potential of free chains does not vary with chain length, if the temperature is high enough. Using the incremental gauge cell, we can confirm this for high temperatures (8, 3.2) and moderate chain lengths (200 monomers). Confining chains above the Θ-temperature results in high entropy, unfavorable conformations, and thus a high chemical potential. When reducing temperature, an interesting behavior of μ_{incr} is observed. Entropic confinement effects are balanced, or overcome, by enthalpic adsorption effects. In the intermediate temperature case, μ_{incr} increases non-linearly as the chain is mostly adsorbed to the pore walls. In the low temperature case μ_{incr} appears to behave similarly the chemical potential of adsorbed simple fluid; the isotherm shows the formation of a monolayer and subsequent pore volume filling with layer. The isotherm forms a van der Waal's type loop when transitioning from layered to pore-filling configurations, similarly to the capillary condensation of simple fluids in mesopores.

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