Thermodynamics Predicts How Confinement Modifies the Dynamics of the Equilibrium Hard-Sphere Fluid

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We study how confining the equilibrium hard-sphere fluid to restrictive one- and two-dimensional channels with smooth interacting walls modifies its structure, dynamics, and entropy using molecular dynamics and transition-matrix Monte Carlo simulations. Although confinement strongly affects local structuring, the relationships between self-diffusivity, excess entropy, and average fluid density are, to an excellent approximation, independent of channel width or particle-wall interactions. Thus, thermodynamics can be used to predict how confinement impacts dynamics.

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The molecular dynamics of fluids confined to small spaces can differ significantly from the bulk. These differences have generated interest because confined fluids feature prominently in both nature and technology. Examples include dynamics of water near proteins or in concentrated cellular environments, transport processes across biological membranes, and fluid flows encountered in micro- or nanofluidic devices, to mention a few. Given that a significant fraction of the molecules in these systems populate highly inhomogeneous interfacial environments, it is easy to appreciate why confinement has nontrivial consequences for their transport coefficients (e.g., diffusivity and viscosity). Nonetheless, a theoretical framework that can reliably predict these consequences has been slow to develop.

One logical starting point is to ask whether confinement induced modifications to equilibrium fluid properties, such as the density, can explain some of the observed differences in dynamics [1–3]. For instance, if the presence of a strongly attractive substrate increases the local fluid density near the fluid-substrate interface, one might naturally expect a corresponding decrease in particle mobility near that interface, and vice versa. This type of argument is physically intuitive, and it has been recently used to rationalize why nanoscale materials exhibit glass transition temperatures that are shifted relative to their bulk values [3]. However, it seems doubtful that average structural quantities alone can account for the wide variety of dynamical behaviors observed in both simulations and experiments of confined fluids [4–6]. As a result, it is natural to ask whether other equilibrium measures, such as the entropy, can provide additional insights. Unfortunately, it is currently difficult to obtain the necessary experimental data for testing these possible connections between thermodynamics and dynamics for confined fluids. Thus, simulation results on simple and well-defined model systems are of great complementary value.

In this Letter, we advance the current understanding of the relation between thermodynamics and dynamics in inhomogeneous systems by addressing the following two questions. (i) Can either the entropy or the average density be used to determine the extent to which confinement alters the diffusivity of a hard-sphere (HS) fluid? (ii) If so, do the specific interactions between particles and the channel boundaries significantly impact the result? While the confined HS system represents arguably the most elementary and well-studied model for inhomogeneous colloidal and molecular fluids, there is still surprisingly little known about the possible connections between its basic thermodynamic and kinetic properties. If such connections do exist and prove to be robust, it suggests that equilibrium theories for inhomogeneous fluids might generally provide important information regarding how confinement modifies the transport properties of fluids.

One reason to speculate that entropy could be a reliable predictor for how confinement affects the diffusivity is its empirical success for capturing the dynamical behavior of bulk materials. In particular, computer simulation studies have demonstrated that the single-component HS and Lennard-Jones fluids, along with a variety of models for liquid metals, exhibit, to a very good approximation, a one-to-one relationship between diffusivity and excess entropy over a broad range of thermodynamic conditions [7–11]. Excess entropy has also been shown to accurately capture the behavior of diffusion phenomena in fluid mixtures [12–14] as well as those in solid-state ionic conductor and quasicrystalline materials [8].

To explain the origin of the correspondence between excess entropy and diffusivity in bulk materials, several researchers have presented independent derivations of apparent scaling laws relating the two quantities. The earliest that we are aware of is due to Rosenfeld and is motivated by a variational thermodynamic perturbation theory [7,9]. Dzugutov later used arguments based on kinetic theory to justify a similar scaling [8], and recently mode-coupling theory has been employed to establish an approximate basis for the observed connection [12,13]. Despite the effort devoted to justifying these scaling laws theoretically and testing their validity for bulk materials, to our knowledge the relationship between excess entropy and diffusivity has never been tested in inhomogeneous fluids, nor has it been used as a tool to understand how confinement affects dynamics.

To carry out such a test, we studied how the structure, thermodynamics, and dynamics of the HS fluid confined to restrictive two-dimensional (2D) or one-dimensional (1D) channels ("films" or "pores," respectively) bounded by smooth, interacting walls differ from those of the bulk system. We considered five 2D channel sizes that were effectively macroscopic in the x and y directions and had particle-center accessible dimensions in the confining z direction of $h_z = 15$, 10, 7.5, 5, and 2.5, respectively. We also considered three 1D channel sizes that were effectively macroscopic in the x direction and had particle-center accessible dimensions in the confining y and z directions of $h_y \times h_z = 7.5 \times 7.5$, 7.5×5, and 5×5, respectively. To simplify notation, we have implicitly nondimensionalized lengths in this study by the HS diameter σ and times by the combination $\sigma\sqrt{m\beta}$, where m is particle mass, $\beta = 1/k_BT$, k_B is Boltzmann's constant, and T is temperature. Consequently, energies are given per unit k_BT. Position-dependent interactions between particles and channel walls $u(\zeta)$ were calculated using a square-well potential:

$$\begin{aligned} u(\zeta) &= \infty & \zeta &< 1/2 \\ &= \epsilon_w & 1/2 \le \zeta &< 1 \\ &= 0 & \zeta &\ge 1, \end{aligned} \tag{1}$$

where ζ represents the shortest distance between a given particle center and the wall of interest, and ϵ_w is the strength of the effective particle-wall interaction. We considered five cases for the 2D channels: $\epsilon_w = 1$ and $\epsilon_w = 0.5$ representing repulsive walls, $\epsilon_w = 0$ representing "hard" but neutral walls, and $\epsilon_w = -0.5$ and $\epsilon_w = -1$ representing attractive walls. Only hard walls were considered for the three highly restrictive 1D channels.

To monitor kinetic processes in these systems, we performed event-driven molecular dynamics simulations [15] in the microcanonical ensemble using $N = 4500$ particles. Periodic boundary conditions were employed in the D "free" directions (i.e., directions not confined by walls). The dimensions of the simulation cell in the periodic directions were set to various values to simulate fluids with different average number densities that span the stable equilibrium range, from the dilute gas to the fluid at its freezing transition. We extracted self-diffusivity D by fitting the long-time ($t \gg 1$) behavior of the average mean-squared displacement to the Einstein relation $\langle \Delta \mathbf{r}_D^2 \rangle = 2DDt$, where $\Delta \mathbf{r}_D^2$ corresponds to the mean-square displacement in the D periodic directions. We also calculated D for several state points with both smaller ($N = 3000$) and larger ($N = 6000$) particle numbers to verify that system size effects in the periodic directions were negligible. For the conditions investigated here, none of the model systems that we consider exhibit anomalous diffusion [16].

We determined the excess entropy per particle s^{ex} using grand canonical transition-matrix Monte Carlo (GC TMMC) simulations [17]. Here, s^{ex} is defined to be the difference between the entropy per particle of the fluid and that of an ideal gas with the same spatial distribution of the particle number density. GC TMMC simulations require fixed values for the activity ξ [18], the particle-center accessible dimensions $\{h_x, h_y, h_z\}$ that define the volume of the simulation cell $V = h_xh_yh_z$, and the reciprocal temperature β. We set $\xi = 1$, $\beta = 1$, and we used the particle-wall interactions given by Eq. (1). The values of $h_y \times h_z$ or h_z were determined by the confining dimensions of the 1D or 2D channels, respectively, and the remaining periodic dimension(s) were chosen to satisfy $V = 1000$. Indistinguishable results were obtained for systems of size $V = 500$.

The key quantities extracted from the GC TMMC simulations were the particle number probability distribution $\Pi(N)$, the excess configurational energy $U^{ex}(N)$, and the N-specific spatial density distribution $\rho(N, \mathbf{r})$, each evaluated over a range of particle numbers spanning from $N = 0$ to $N = 984$. Using arguments from statistical mechanics [19,20], one can relate these quantities to s^{ex} for the inhomogeneous HS fluid:

$$\begin{aligned} s^{ex}(N)/k_B = N^{-1}\{&\ln[\Pi(N)/\Pi(0)] - N\ln\xi + \ln N! \\ &- N\ln N + \beta U^{ex}(N) + \int \rho(N, \mathbf{r}) \\ &\times \ln\rho(N, \mathbf{r})d\mathbf{r}\}. \end{aligned} \tag{2}$$

Given that $V = 1000$ is fixed, Eq. (2) provides $s^{ex}(\rho_h)$ within the range $0 \le \rho_h \le 0.984$, where $\rho_h = N/V$ is the number density based on the particle-center accessible volume.

First, we discuss our observations for the utility of s^{ex} in predicting how confinement affects dynamics. Figure 1 shows a parametric plot of D versus $-s^{ex}$ for the HS fluid both in the bulk and confined to the 17 different 2D channels ($h_z = 2.5, 5, 10$ with $\epsilon_w = 1, 0.5, 0, -0.5, -1$ and $h_z = 7.5, 15$ with $\epsilon_w = 0$). The data, which encompass the dynamic behavior of the equilibrium fluid from the dilute gas to the freezing transition, span three decades in D. The collapse of the data onto a single master curve indicates that, to an excellent approximation, the one-to-one correspondence between D and s^{ex} for the bulk fluid also holds when it is severely confined. The quality of the collapse is largely independent of either channel width (including "particle-scale" channels with $h_z = 2.5$) and the sign or magnitude of the particle-wall interaction. Data for the HS fluid confined to the 3 rectanglular 1D channels described above are superimposed in the inset of Fig. 1. As

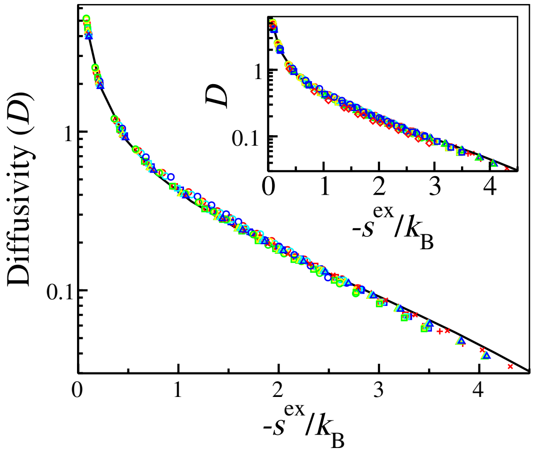

FIG. 1 (color online). Self-diffusivity D vs the negative of excess entropy per particle $-s^{\mathrm{ex}}/k_{\mathrm{B}}$ for the bulk HS fluid (solid curve) and for the HS fluid in 2D channels (symbols). The symbols correspond to $h_z = 2.5$ (circle), 5 (square), 7.5 (plus), 10 (triangle up), and 15 (cross). The color codes are $\epsilon_{\mathrm{w}} = 1$ (blue), 0.5 (cyan), 0 (red), -0.5 (yellow), and -1 (green). Inset is the same plot with added points for the 1D channels: 5×5, 7.5×7.5, and 5×7.5 shown by red diamonds.

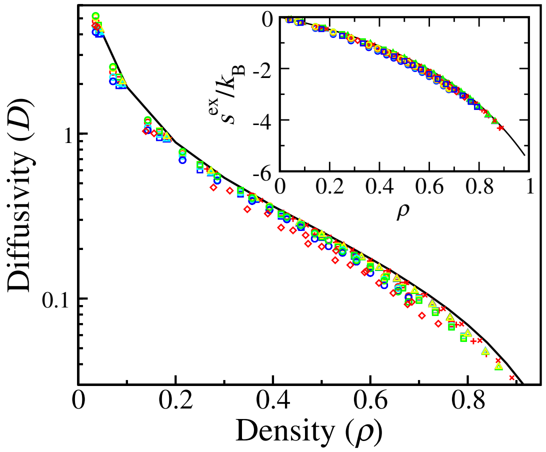

FIG. 2 (color online). Self-diffusivity D and excess entropy per particle $s^{\mathrm{ex}}/k_{\mathrm{B}}$ vs average density $\rho = N/V'$ based on the total system volume V'. Systems shown include the bulk HS fluid (solid curve) and the HS fluid confined to the 1D and 2D channels (symbols) discussed in the text. Symbols are identical to those given in Fig. 1.

can be seen, they also approximately collapse onto the bulk relationship between D and s^{ex}. In fact, diffusivities for approximately 50%, 70%, and 90% of the confined state points shown in Fig. 1 are within 3%, 5%, and 10%, respectively, of the bulk value at the same excess entropy.

Having established that s^{ex}, an equilibrium thermodynamic property, can be used to predict how various confining environments impact D, it is natural to press forward and ask whether the same predictive information is contained within an even simpler structural measure: the average density. Here, one needs to be specific because there are two different definitions of average density that are commonly used to characterize inhomogenenous HS fluids ($\rho_h = N/V$ and $\rho = N/V'$). The former is based on the particle-center-accessible volume $V = h_x h_y h_z$, while the latter is based on the total system volume, i.e., $V' = V$ for bulk systems, $V' = h_x h_y (h_z + 1)$ for 2D channels, and $V' = h_x (h_y + 1)(h_z + 1)$ for 1D channels. Schmidt and Löwen [21] and, later, Zangi and Rice [22] demonstrated that ρ is in fact the relevant density for the lateral (i.e., periodic) component(s) of the pressure tensor, and thus ρ is also a natural independent variable for the free energy of the system. Below, we investigate whether ρ is also an accurate predictor for how confinement effects D.

Figure 2 shows both D and s^{ex} as a function of ρ for the bulk HS fluid as well as for the HS fluid confined to the 2D and 1D channels. The collapse of the data, while not perfect, demonstrates very strong correlations between D, s^{ex}, and ρ that are nearly independent of the confining dimensions and the particle-wall interactions. Approximately 70% and 90% of the diffusivities for the confined state points shown in Fig. 2 are within 10% and 20%, respectively, of the bulk value at the same ρ. This is another significant result because, unlike s^{ex}, ρ is intuitively simple to understand and trivial to determine in simulations (e.g., it is specified in microcanonical and canonical simulations). As expected, the systems that exhibit the most noticeable deviation from bulk behavior in Fig. 2 are the ones for which the fluid is under the most severe confinement, i.e., channels with dimensions comparable to the particle diameter. In these cases, it appears that specific fluid structuring (e.g., density enhancements in the channel corners) acts to only slightly reduce the diffusivity relative to what would be predicted by the average density ρ.

Given the approximate collapse of the data in Fig. 2, it is natural to wonder whether it is simply the particle structuring that is determining the HS dynamics. To test this idea further, we examine in Fig. 3 the local density profiles $\rho(z)$ for a HS fluid confined to 2D channels of width $h_z = 2.5$ but with three different particle-wall interactions: $\epsilon_{\mathrm{w}} = 1$ (repulsive), $\epsilon_{\mathrm{w}} = 0$ (neutral), and $\epsilon_{\mathrm{w}} = -1$ (attractive). All three systems exhibit the same average density ρ, and thus according to Fig. 2, display approximately the same D as the bulk. Clearly there are real and pronounced differences in the local structuring of the three confined fluids, especially when compared to the uniform bulk material. These types of differences do generally impact the entropy and are the main focus of studies of inhomogenenous fluids by classical density functional theories. However, since the excess entropy (the quantity which correlates strongly with D) measures the difference between the system of interest and an ideal gas with the same spatial particle distribution [20], one can perhaps appreciate why both s^{ex} and D are fairly insensitive to the details of the density profile.

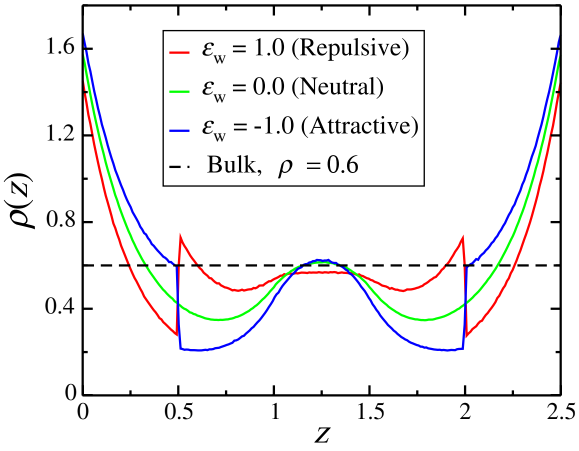

FIG. 3 (color online). Density profiles $\rho(z)$ for HS fluids confined to a 2D channel of width $h_z = 2.5$. Although each system has different particle-wall interaction strengths ϵ_w, they share a common average density ρ (dashed) and self-diffusivity D.

Finally, we examine what conclusions regarding density follow if one instead chooses to plot D versus the alternative definition for average density, $\rho_h = N/V$, based on the total particle-center-accessible volume V. In particular, Fig. 4 compares D for the HS fluid confined to 5 different 2D channels with hard walls ($\epsilon_w = 0$) as a function of ρ_h. Unlike when plotting versus ρ, there is no data collapse in this case. Thus, one might consider ρ a more natural independent variable than ρ_h, not only for thermodynamics of inhomogeneous fluids [21,22], but also for dynamics.

To conclude, we have probed the structure, entropy, and diffusivity of the equilibrium HS fluid confined to 2D and 1D channels with a wide range of dimensions and particle-boundary interactions. Our main finding is that the relationships between D, s^{ex}, and ρ for the bulk fluid also remain valid, to within an excellent approximation, when the fluid is confined to particle-scale geometries. Since statistical mechanical theories can provide accurate estimates for how confinement modifies s^{ex}, the robust connection between thermodynamics and dynamics reported here should have far-reaching implications for the prediction of dynamics in confined systems. We are currently testing whether similar connections hold (i) for the metastable HS fluid, (ii) for the equilibrium HS fluid in more general random environments (e.g., quenched media), and (iii) for fluids with strong interparticle attractions that significantly affect local structuring.

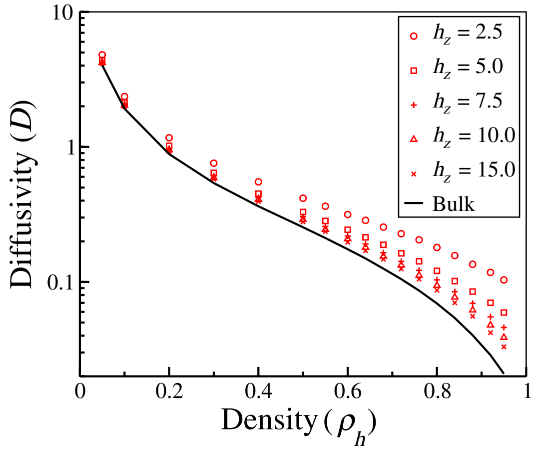

FIG. 4 (color online). Self-diffusivity D vs average density $\rho_h = N/V$ based on the total particle-center-accessible volume V. Systems shown include the bulk HS fluid (solid curve) and the HS fluid confined to the 2D channels between hard walls.

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