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Using compressibility factor as a predictor of confined hard-sphere fluid dynamics

Jeetain Mittal*

Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20892-0520, USA

Abstract

We study the correlations between the diffusivity (or viscosity) and the compressibility factor of bulk hard-sphere fluid as predicted by the ultralocal limit of the barrier hopping theory. Our specific aim is to determine if these correlations observed in the bulk equilibrium hard-sphere fluid can be used to predict the self-diffusivity of fluid confined between a slit-pore or a rectangular channel. In this work, we consider a single-component and a binary mixture of hard spheres. To represent confining walls, we use purely reflecting hard walls and interacting square-well walls. Our results clearly show that the correspondence between the diffusivity and the compressibility factor can be used along with the knowledge of the confined fluid's compressibility factor to predict its diffusivity with quantitative accuracy. Our analysis also suggests that a simple measure, the average fluid density, can be an accurate predictor of confined fluid diffusivity for very tight confinements (≈ 2 -3 particle diameters wide) at low to intermediate density conditions. Together, these results provide further support for the idea that one can use robust connections between thermodynamic and dynamic quantities to predict dynamics of confined fluids from their thermodynamics.

Introduction

The behavior of fluids in small spaces, with one of the characteristic dimensions of the order of few fluid particle diameters, can be significantly different from the bulk. Some of the well-studied features of such confined fluids are the formation of layering structure normal to the confining walls,¹ inhomogeneous pressure equation of state,¹ appearance of surface induced phase transitions,^{2,3} and shift in the glass transition temperature.^{4,5} The scientific progress on some of the issues related to the behavior of confined fluids has been biased towards understanding the structural changes and associated thermodynamic properties due to confinement. In fact, now we have theories at our disposal which can predict the implications of confinement on the thermodynamic properties quantitatively over a wide range of conditions.⁶ On the contrary, the situation is not so satisfactory for predicting the dynamic behavior (such as the average self-diffusivity) of confined fluids.⁷⁻⁹ One of the reasons for this slow advancement on understanding fluid dynamics under confinement is the lack of tractable kinetic theories even for the bulk fluid behavior over the whole equilibrium fluid range.

Recent studies have utilized a different strategy to predict the transport properties of fluids under confinement; their aim is to find empirical correlations between thermodynamic and dynamic quantities which remain approximately unchanged due to confinement.¹⁰⁻¹² The thermodynamic quantity used to find such correlations can be as simple as the average fluid density,¹⁰ although significantly better results are obtained by using quantities such as the

jeetain@helix.nih.gov.

excess entropy^{10,11,13,14} of the fluid with respect to the ideal gas state and the available volume.^{12,15} The idea is to utilize these correlations obtained from the bulk fluid behavior along with the information about the thermodynamic property of confined fluids (which can be easily obtained via theory, molecular simulation, or laboratory experiment) to calculate the dynamic quantity with quantitative accuracy. This line of enquiry seems rather promising from the studies so far on equilibrium fluids as one can predict the effect of confinement on the self-diffusivity (or alternatively shear viscosity which follows trivially from the Stokes-Einstein relationship for equilibrium fluids) for a wide range of fluid models such as hard-sphere, Lennard-Jones (LJ), square well and others by utilizing “excess entropy-diffusivity”^{10,11} and “available volume-diffusivity”¹² bulk relationships.

The possible explanation for the observed correlations between these quantities of seemingly different origin (thermodynamic versus dynamic) even in the bulk has mostly been qualitative and there is no first principle based justification available. It has been argued that excess entropy should naturally be a quantity which will track the fluid dynamics as it characterizes the reduced number of states due to interparticle correlations.¹⁶ But it is not clear what the functional relationship should be^{17,18} and if there is a universal connection or something more like a parameteric fit with fitting coefficients dependent on the state of the fluid (density, temperature) and the type of fluid (strong versus fragile). Whether these correlations persist in the supercooled state is also somewhat an open question¹⁹ with previous work pointing towards the need for an additional adjustable parameter (as a function of density in case of binary Lennard-Jones²⁰ and SPC/E water²¹).

In this regard, recent results from the single particle barrier hopping theory of Schweizer and co-workers²² may be an important step towards bridging the gap between observations and fundamental understanding. One specific result out of many predictions made by this theory is that the relaxation time (or inverse diffusivity D) for the bulk hard-sphere fluid should scale with the compressibility factor $Z = \beta P/\rho$ as,²³

$$\frac{D}{D_0} \propto \exp(a\varphi^{-1}(Z-1)^2), \quad (1)$$

where $\beta = [k_B T]^{-1}$, k_B is the Boltzmann constant, T is temperature, P is pressure, ρ is the fluid density, D_0 is an elementary diffusion scale, a is a numerical prefactor, $\varphi = \pi\rho\sigma^3/6$ is the fluid packing fraction, and σ is the fluid diameter. A qualitative agreement with the predictions of eq 1 was already found in a previous work on the dynamics of polydisperse hard-sphere fluid which showed that the relaxation time as a function of Z for several different polydispersity values can be approximately collapsed onto a single curve.²⁴ A quantitative comparison of eq 1 with the actual diffusion data will provide a useful starting point for understanding some of the outstanding issues related to the dynamics of supercooled fluids. As the focus of this paper is the equilibrium fluid dynamics under confinement, we will only touch upon this issue very briefly in the beginning of results and discussion section. Detailed results and the discussion on the supercooled fluid behavior from the perspective of eq 1 will be provided in a future publication.

Here, instead we focus on the possibility of D - Z relationship as observed in the bulk for an equilibrium hard-sphere fluid as a predictor of diffusion under confinement by utilizing the knowledge about its Z . For confined systems, pressure is a tensorial quantity (and therefore Z) and for a slit-pore system (fluid confined between walls in one direction) pressure has two components, parallel and normal to the walls. For average diffusion parallel to the walls (which will be the main dynamic quantity of interest in this work), we expect that the compressibility

factor based on the average pressure component in the parallel direction will be relevant. As our fluid models, we consider both a single-component and a binary mixture of hard-sphere particles. For confinement models, we consider slit-pore geometry with hard walls and attractive square-well walls and rectangular channels with hard walls. We find that the bulk D - Z relationship remains essentially unchanged due to these different types of confinement and can be successfully used to predict the diffusivity of confined fluids with quantitative accuracy for most of the state points. We further notice that any expected deviations from the exact diffusion values are generally negative (under-prediction) for low to intermediate density states and positive (overprediction) for high density states. Data from previous studies show that qualitatively similar deviations are expected from the excess entropy - diffusivity and available volume - diffusivity correlations.¹² An attractive aspect of our observed correlation between the compressibility factor and diffusivity, as compared to previous work on other thermodynamic measures, is that one can calculate Z fairly easily using colloidal hard sphere experiments in bulk (and possibly under confinement with appropriate modifications in the analysis)²⁵ and in molecular simulations.

Simulation details

We have used discontinuous molecular dynamics (DMD) simulations²⁶ to track various thermodynamic and dynamic properties of the hard-sphere (HS) fluid model. The DMD simulations each involved $N = 10000$ HS particles contained within a simulation cell of volume $V = H_x \times H_y \times H_z$, where H_i is the box length in a given direction ($i = x, y, z$). Periodic boundary conditions were applied in all three directions for bulk and in two directions (x and y) for the slit-pore, and in one direction (x) for the rectangular channel. The non-periodic directions in case of confined fluids can be either smooth “hard” walls which are perfectly reflecting or “attractive” walls with a square-well potential between the fluid particles and the confining walls,

$$u(z) = \begin{cases} \infty & z < \sigma/2 \\ -\epsilon_w & \sigma/2 \leq z < \sigma \\ 0 & z \geq \sigma, \end{cases} \quad (2)$$

where z 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 only consider hard walls in case of rectangular channels.

The diffusivity D of the fluid was obtained by fitting the long-time behavior of the average mean-squared displacement of the particles to the Einstein relation $\langle \Delta r_d^2 \rangle = 2dDt$, where $\langle \Delta r_d^2 \rangle$ corresponds to the mean-square displacement per particle in the d periodic directions after time t . To calculate the compressibility factor Z , we use the following form of the virial theorem,^{27,28}

$$Z = 1 + \frac{m \sum_{\text{collisions}} (\mathbf{r}_{ij} \cdot \Delta \mathbf{v}_i)}{dNk_B T t_e}, \quad (3)$$

where $\mathbf{r}_{ij}$ is the position vector between particles i and j , $\mathbf{v}_i$ is the change in velocity of particle i after the collision, N is the number of particles, and the summation is over all the collisions during the elapsed time t_e . In case of confined systems, the vector product includes only the periodic components of $\mathbf{r}_{ij}$ and $\mathbf{v}_i$ for Z parallel to the walls and non-periodic components for

Z normal to the walls. We test our Z calculations against the GC-TMMC simulation results^{29,30} and find favorable comparison for both bulk and confined systems (less than 0.5%) difference.^{13,14} To simplify the notation in this paper, we have implicitly non-dimensionalized all quantities by appropriate combinations of a characteristic length scale (which we take to be the HS particle diameter σ) and time scale (which we choose to be $\sigma \sqrt{m\beta}$, where m is particle mass). As a result, all quantities with dimensions of energy are understood to be “per $k_B T$ ”, the only energy scale in the problem.

Results and discussion

Bulk hard-sphere fluid

First we check the predictions of eq 1 for the bulk HS fluid. Although the barrier hopping theory in its ultralocal limit is expected to be valid for strongly supercooled liquids,²³ we want to see if this can also provide some reasonable predictions for weakly supercooled and equilibrium fluid states. As we are using a monatomic fluid which is hard to supercool and will crystallize readily, it is not possible to access strongly supercooled regime. Figure 1 shows the D data plotted against ϕ (top panel) as well as $(Z-1)^2/\phi$ (bottom panel) as expected from eq 1 for $\phi \leq 0.53$. We are able to fit the data for most of the dense fluid range ($D < 0.1$ and $\phi > 0.40$) to eq 1. Equation 1 is only valid for fluid states above the ideal glass transition packing fraction ($\phi_i = 0.432$) at which the activated barrier hopping dynamics becomes important²² and the deviations seen in Figure 1 at low density are therefore expected. We also show the inverse viscosity $1/\eta$ on the same plot and the expected fit from the Stokes-Einstein relationship, i.e., $D\eta = 1/2\pi$ in the bottom panel. To verify that the fluid systems between $\phi = 0.49$ to $\phi = 0.53$ are not phase separated (as coexistence between the fluid-solid phase for the HS model is between $\phi = 0.494$ – 0.545),³¹ we check the time evolution of Z as well as several other order parameters, e.g., bond-orientation order Q_6 ,³² pair-correlation function $g(r)$, translational order parameter s_2 ³³ and do not find any evidence of phase separation at the time scale of the simulations. Of course, if we run the simulations for long enough, these state points will show fluid and solid phases in coexistence. We use a similar approach to identify stable and metastable (at the simulation timescales) state points for the confined HS system for which the location of the fluid-solid phase boundary may not be known apriori. In future we will investigate whether the trends observed here also hold in the deeply supercooled state by utilizing a polydisperse HS fluid to avoid crystallization.

Next, we want to examine if the correspondence between D and Z observed in the bulk is unchanged due to confinement and can therefore be used as a predictive tool for confined fluid diffusivity. To facilitate this process, we fit our bulk data to an analytic functional form³⁴ $D = f(Z)$ as shown in the inset of Figure 1. To simplify the analysis we have used D – Z relationship but D – $(Z-1)^2/\phi$ can also be used for rest of the analysis in this paper. Further, we plot the ratio of the actual DMD data and $f(Z)$ to assess the reliability of our fit, and find overall good agreement with less than 5% error for $Z > 5$. From now onwards we will use $f(Z)$ as a functional representation of our bulk D data.

Hard-sphere fluid confined between hard walls

First, we test the effect of hard-wall confinement on the D – Z relationship. Figure 2 shows the data for bulk HS (solid line), HS confined between slit-pores of size $H = H_z$, and rectangular channels with dimensions $H_y \times H_z$. Overall, the collapse of confined fluid data on the bulk curve is good suggesting that $f(Z)$ can be used as a predictor of diffusivity if Z for the confined fluid is known. For more restrictive confinements, e.g., in rectangular channels and for a slit-pore of size $H = 4$, D – Z curves have a different slope from the bulk curve which gives rise to underprediction in D from $f(Z)$ at intermediate Z and overprediction in D at high Z as shown

in the inset of Figure 2. The Z -range (or alternatively ϕ -range) considered here covers most of the equilibrium state points as known from the exact fluid-solid phase diagram.³⁵

Hard-sphere fluid confined between attractive walls

To test if D - Z correspondence is still valid when we introduce fluid-wall interactions, we calculate these quantities for systems with varying attraction strength ε_w (eq 2). Figure 3 shows the bulk HS data (line) along with the confined fluid data (symbols) which demonstrates that indeed the D - Z relationship remains unchanged. To assess quantitative differences, we plot $D/f(Z)$ in the inset of Figure 3 which shows that difference between the bulk and confined diffusivity based on Z is less than 10% for 75% of the state points and always less than 15%.

Binary mixture of hard-sphere fluid confined between hard walls

As most of the fluid systems of practical interest are not single-component but rather a mixture of different sizes, it will be instructive to investigate if the D - Z relationship can also be useful for predicting the diffusivity of equilibrium confined fluid mixtures. We have simulated a binary mixture of hard spheres with particle size ratio given by $\sigma_2/\sigma_1 = 0.75$ and equal mass ($m_2 = m_1$). We present data for two mixture compositions, equal particle numbers ($N_1 = N_2 = 5000$) and equal packing fraction ($N_1 = 2967, N_2 = 7033; \phi_1 = \phi_2$). Figure 4 shows the diffusivity D_i for both the components ($i = 1$ (black lines and symbols) and $i = 2$ (red lines and symbols)) as a function of Z in bulk (equal particle numbers: solid lines, equal packing fraction: dashed lines) and confined in a slit-pore of size $H = 5$ (equal particle numbers: filled symbols, equal packing fraction: empty symbols). Again, we find a one-to-one correspondence between the bulk and confined D - Z relationship thereby suggesting that Z can be a reliable predictor of confined fluid diffusivity for fluid mixtures. We fit individual component data for the equimolar mixture in the bulk to an analytic functional form³⁴ $D_i = f_i(Z)$ to facilitate comparison with the confinement data. This will also help in assessing the dependence of observed correlations on the mixture composition. To quantify the differences between the actual DMD data and predictions based on the bulk $f_i(Z)$ and the confined fluid Z , we plot $D_i/f_i(z)$ in the inset of Figure 4. It is clear that the confinement data for an equimolar mixture is quantitatively described by the bulk relationship based on the same mixture composition but the prediction for a different composition (equal packing fraction) is only semi-quantitatively described at high Z (or alternatively high ϕ).

Frustrated dynamics due to imperfect layering

It was observed in a previous work that the formation of layering structure normal to the walls can actually facilitate the motion in both parallel¹⁴ and normal¹⁵ directions. Similarly, frustrated layering formation due to pore-sizes which cannot accommodate an integer number of layers can impede the particle motion or its diffusivity. These observations were utilized to propose a possible route to control mobility in small channels by modifying the wall-particle interactions to impose a predetermined density profile and thereby achieve the required D .³⁶ For a HS fluid confined between hard walls, it was found that the fluctuations in D as a function of H for a given packing fraction can be explained by a similar change in the excess entropy of the fluid.¹⁴ But the excess entropy in this case was only able to provide a semi-quantitative measure of dynamics as seen by an imperfect collapse of confinement data on the bulk diffusivity-excess entropy curve at high ϕ . Later, it was shown that the available volume can provide a better description of this data and make improved predictions.¹²

Here, we test if D - Z correlations can describe the layering induced fluctuations in confined fluid D qualitatively and further quantitatively. Figure 5 shows the diffusivity data for HS between hard walls as a function of varying H along various isochores. Symbols are the actual simulation data and solid lines are the predictions based on bulk data ($f(Z)$) and the confined fluid Z . Overall, we find that the predictions match well with the actual data, especially for

high ϕ the agreement is remarkable as opposed to the predictions based on excess entropy.¹⁴ Moreover, low to intermediate ϕ data can actually be described simply based on the average packing fraction as it matches the bulk diffusivity at the same ϕ (shown by horizontal dashed lines) very well.

Conclusions

We have shown that the relationship between a thermodynamic and a dynamic quantity, i.e., between “diffusivity and compressibility factor” can be used to predict the effect of confinement on fluid diffusivity. Along with the knowledge of bulk D – Z relationship, the information about the confined fluid's compressibility factor is needed which can be easily estimated from experiments or approximated using existing theoretical approaches such as the density functional theory. This provides an indirect but quantitative route to predict confined fluid diffusivity based on its thermodynamics. One of the interesting features about the observed D – Z correlations is that the barrier hopping theory for supercooled fluid dynamics in its ultralocal limit predicts such an expectation for a bulk hard-sphere fluid and a precise functional form for these correlations. We find that this expected functional dependency is satisfied for a single-component hard-sphere fluid in a weakly supercooled state and even in the equilibrium fluid state. In future work, we will focus on understanding the D – Z correlations for supercooled fluids in bulk and under confinement by utilizing polydisperse fluids to thwart crystallization and size segregation. We are currently also investigating if D – Z correlations can be used to predict the effect of confinement on dynamics for attractive fluids with square-well or Lennard-Jones interactions.

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References

1. Davis, HT. Statistical Mechanics of Phases, Interfaces, and Thin Films. VCH; 1996.
2. Gelb LD, Gubbins KE, Radhakrishnan R, Sliwinski-Bartkowiak M. Rep Prog Phys 1999;62:1573.
3. Sellers MS, Errington JR. J Phys Chem C 2008;112:12905.
4. Alcoutlabi M, McKenna GB. J Phys: Condens Matter 2005;17:R461.
5. Mittal J, Shah P, Truskett TM. J Phys Chem B 2004;108:19769.
6. Hansen, JP.; McDonald, IR. Theory of Simple Liquids. Vol. 3rd. Academic Press; 2006.
7. Magda JJ, Tirrell MV, Davis HT. J Chem Phys 1985;83:1888.
8. Vanderlick TK, Davis HT. J Chem Phys 1987;87:1791.
9. Krishnan SH, Ayappa KG. J Phys Chem B 2005;109:23237. [PubMed: 16375288]
10. Mittal J, Errington JR, Truskett TM. Phys Rev Lett 2006;96:177804. [PubMed: 16712334]
11. Mittal J, Errington JR, Truskett TM. J Phys Chem B 2007;111:10054. [PubMed: 17629320]
12. Goel G, Krekelberg WP, Pond MJ, Mittal J, Shen VK, Errington JR, Truskett TM. J Stat Mech 2009:P04006.
13. Mittal J, Shen VK, Errington JR, Truskett TM. J Chem Phys 2007;127:154513. [PubMed: 17949179]
14. Mittal J, Errington JR, Truskett TM. J Chem Phys 2007;126:244708. [PubMed: 17614578]
15. Mittal J, Errington JR, Truskett TM, Hummer G. Phys Rev Lett 2008;100:145901. [PubMed: 18518049]

16. Dzugutov M. Nature 1996;381:137.
17. Rosenfeld Y. Phys Rev A 1977;15:2545.
18. Rosenfeld Y. J Phys: Condens Matter 1999;11:5415.
19. Dzugutov M. Phys Rev E 2002;65:032501.
20. Mittal J, Errington JR, Truskett TM. J Chem Phys 2006;125:076102. [PubMed: 16942382]
21. Mittal J, Errington JR, Truskett TM. J Phys Chem B 2006;110:18147. [PubMed: 16970429]
22. Schweizer KS, Yatsenko G. J Chem Phys 2007;127:164505. [PubMed: 17979358]
23. Schweizer KS. J Chem Phys 2007;127:164506. [PubMed: 17979359]
24. Sear RP. J Chem Phys 2000;113:4732.
25. Dullens RPA, Arts DGAL, Kegel WK. Proc Natl Acad Sc 2006;103:529. [PubMed: 16407150]
26. Rapaport, DC. The Art of Molecular Dynamics Simulation. Vol. 2nd. Cambridge University Press; 2004.
27. Alder BJ, Wainwright TE. J Chem Phys 1959;31:459.
28. Denlinger MA, Hall CK. Mol Phys 1990;71:541.
29. Errington JR. J Chem Phys 2003;118:9915–9925.
30. Errington JR, Shen VK. J Chem Phys 2005;123:164103. [PubMed: 16268677]
31. Anderson VJ, Lekkerkerker HNW. Nature 2002;410:811. [PubMed: 11976674]
32. Steinhardt P, Nelson DR, Ronchetti M. Phys Rev B 1983;28:784.
33. Truskett TM, Torquato S, Debenedetti PG. Phys Rev E 2000;62:993.
34. $f(Z) = (a + bZ + cZ^2 + dZ^3)/(1 + eZ + fZ^2 + gZ^3)$, where a, b, c, d, e, f, g are constants.
35. Fortini A, Dijkstra M. J Phys: Condens Matter 2006;18:L371.
36. Goel G, Krekelberg WP, Errington JR, Truskett TM. Phys Rev Lett 2008;100:106001. [PubMed: 18352209]

Figure 1.

Bulk data. (Top panel) Diffusivity D and inverse viscosity $1/\eta$ data are plotted as a function of ϕ . (Bottom panel) Diffusivity D and inverse viscosity $1/\eta$ data are plotted as a function of $(Z-1)^2/\phi$ along with a fit to eq 1. The inset shows D versus compressibility factor Z along with a fit to the DMD data with function $f(Z)$.³⁴ To ascertain the accuracy of the fit $f(Z)$, ratio of the DMD data to the fit $f(Z)$ is also shown.

Figure 2. Hard wall confinement. Diffusivity D versus compressibility factor Z for hard-sphere fluid in bulk (line) and confined between hard-walls (symbols). The ratio $D/f(Z)$ as a function of Z is also shown in the inset.

Figure 3. Attractive wall confinement. Diffusivity D versus compressibility factor Z for hard-sphere fluid in bulk (line) and confined between attractive walls represented by a square-well potential eq. 2 (symbols). The ratio $D/f(Z)$ as a function of Z is also shown in the inset.

Figure 4.

Binary hard-sphere mixture. Diffusivity D_i versus compressibility factor Z for a binary mixture of hard spheres in bulk (equal particle numbers: solid lines, equal packing fraction: dashed lines) and confined between hard walls (equal particle numbers: filled symbols, equal packing fraction: empty symbols). Black lines and symbols represent data for component $i = 1$ and red lines and symbols represent data for component $i = 2$. The ratio $D_i/f_i(Z)$ as a function of Z is also shown in the inset, where $f_i(Z)$ is a fit to the bulk equimolar mixture data.

Figure 5.

Layering induced dynamics. Diffusivity D versus slit-pore size H for hard-sphere fluid confined between hard walls. The molecular dynamics data is shown by symbols and the predictions based on bulk diffusivity-compressibility factor relationship is shown by solid lines. The dashed lines are the bulk data at a given packing fraction ϕ .