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Effect of a Distribution of Pore Dimension on Levitation Effect[†]

A. V. Anil Kumar[‡] and Subramanian Yashonath^{*,‡,§,||}

Solid State and Structural Chemistry Unit, and Supercomputer Education and Research Centre, Indian Institute of Science, Bangalore, India 560 012

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Existence of levitation effect in noncrystalline porous solids is verified by means of molecular dynamics simulations. By introducing a normal distribution (characterized by the half-width at half-maximum, $\sigma_G = 0.1$ and 0.5 \AA) of 12-ring window diameters disorder is introduced in crystalline faujasite. Investigation of motion of spherical sorbates within this disordered host suggests that levitation effect persists though the intensity of the anomalous peak is reduced compared to crystalline faujasite. In the disordered host there is a breakdown of the linear relationship between the self-diffusivity D and $1/\sigma_{gg}^2$, where σ_{gg} is the sorbate diameter. The activation energy is lowest and the energy barrier is negative for the particle whose sorbate diameter corresponds to the anomalous regime for most window diameters, σ_w , while for the sorbate whose diameter lies in the linear regime, the energy barrier is always positive.

I. Introduction

Atoms diffusing within the pores of a host solid exhibit an unexpected behavior:¹ initially, for small values of the sorbate diameter σ_{gg} , the self-diffusion coefficient, D , decreases with increase in σ_{gg} over a wide range, showing a linear proportionality with $1/\sigma_{gg}^2$, while for large σ_{gg} , D exhibits a peak (see Figure 1). The range of σ_{gg} over which $D \propto 1/\sigma_{gg}^2$ is termed the linear regime, and the region where the peak appears is termed the anomalous regime. The linear proportionality of D with $1/\sigma_{gg}^2$ is expected since the number of collisions will be proportional to the cross section of the particle. This behavior was initially found in zeolites with cage-like structures such as faujasites and zeolite A.^{1,2} Later investigations found that this effect (often called the levitation effect) is also found in zeolites with altogether different pore structures such as simple cylindrical pores found in VPI-5 or a combination of intersecting straight and sinusoidal cylindrical channels found in silicalite³ among others. Derouane and co-workers from an analysis of the effects of the surface curvature predicted that under certain conditions, the adsorbed molecules will exhibit supermobility.⁴

All these studies have one thing in common: they all have been carried out on crystalline zeolites. The pore structure in these crystalline solids can be characterized by well-defined and a single or a few precisely defined pore sizes. Therefore, these studies suggest that the levitation effect exists whenever a diffusing species is moving in a porous *crystalline* solid irrespective of the nature of the void structure. The analysis of Derouane also assumed that the structure of the host through which the sorbates diffuse are crystalline solids with regularly shaped voids.

There are many materials in nature that are noncrystalline and porous. Examples of such systems are Vycor glass, gels, charcoal, and amorphous silica among others.^{5–7} In these noncrystalline porous systems, one finds a distribution of pore

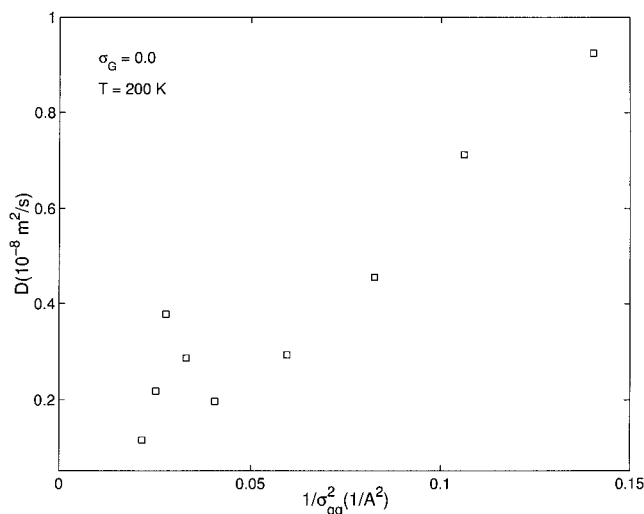


Figure 1. D vs $1/\sigma_{gg}^2$ plot in the case of $\sigma_G = 0$, at $T = 200 \text{ K}$.

dimensions instead of what is found in crystalline porous solids, viz., a single or a set of few well-defined dimensions of pores. Diffusion of guest species within such amorphous porous solids is of great interest, as it is fundamentally important. Also, many amorphous solids are used in technological applications such as batteries and are potential materials for other engineering applications such as storage of gas. For these and other reasons, it is worthwhile to understand diffusion in these amorphous porous solids.

Recently it has been shown that a better separation of the mixtures of different sized molecules can be achieved through the use of an anomalous regime.⁸ Will the levitation effect persist in the absence of a well-defined and precise pore dimension? If one finds a monotonic variation of D with σ_{gg} over the whole range and not what is shown in Figure 1, then in this case such exploitation of the anomalous regime for separation of mixtures would be necessarily restricted to the use of crystalline solids as host materials. Consequently, noncrystalline porous solids will then not compete with crystalline porous solids as candidates for possible use as hosts in separation. If the anomalous peak persists when there is a distribution of pore dimensions,

[†] Publication No. 1516 from Solid State and Structural Chemistry Unit.

[‡] Solid State and Structural Chemistry Unit.

[§] Supercomputer Education and Research Centre.

^{||} Also at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

$f(d_p)$, instead of a single or a few precisely defined pore dimensions, then this would imply that the levitation effect itself is more general than hitherto demonstrated. Also this would have important implications for diffusion of atoms within porous amorphous solids. Further, this would imply that amorphous porous solids could possibly be used as hosts for separation in petrochemical and other industries. Finally, there are many biological materials (for example, biomembranes) that cannot be strictly considered crystalline but that act as hosts for conduction of ions and diffusion of other biologically important molecules. The implications of the existence of an anomalous peak in noncrystalline porous solids on these processes can be several.

Here, with these in view, we undertake to investigate the dependence of self-diffusivity, D , on the sorbate diameter, σ_{gg} , in systems with a distribution of pore dimensions, $f(d_p)$. Since the structures of noncrystalline solids are more difficult to characterize and there are no precise structure determinations reported in the literature (as far as we know), we had to resort to randomization of known crystalline porous solid to generate a noncrystalline porous solid for the purposes of the present study. This is discussed in the next section. We have carried out classical molecular dynamics (MD) studies on these systems. The results of the simulations are presented and discussed in the last section. Finally, implications of the findings and possible applications are outlined.

II. Model and Methods

To investigate diffusion of sorbates in a porous amorphous solid, the structure of the disordered must be known. In a preliminary study such as the present investigation, it is also useful if the degree of disorder of the porous solid is controlled and systematically varied. However, nonavailability of precise structural details of any noncrystalline porous solid in the literature and the need to control the degree of disorder have led us to take a crystalline solid and introduce disorder in it. Before one can do this, one needs a measure of the degree of disorder in noncrystalline porous solids. Earlier Dussert et al.⁹ and Yashonath and Bhasu¹⁰ have shown that one such measure of the degree of disorder is the standard deviation in distances between pairs of atoms. In the present context, where we are dealing with porous solids, by degree of disorder we mean the disorder associated with the pore size distribution. One therefore can reasonably take the width of the pore size distribution, $f(d_p)$, as a measure of the degree of disorder. In a crystalline porous solid such as a zeolite, there is a finite number of well-defined pore sizes. Here the degree of disorder may be taken as zero or near zero.

We found that only the pore size distribution seems to be known for some noncrystalline solids and no details of connectivity of the voids are known. Such information is necessary in a study such as the one planned here. After considerable search for suitable host material, we selected faujasite as our host material. The structure of this is well-known.¹¹ We introduce disorder in this solid in a systematic way. The disorder can be introduced by altering the dimensions of the α -cages or supercages or the dimension of the 12-ring window interconnecting the α -cages. We have chosen to employ the latter, viz., alter the diameter of the 12-ring window. We introduce a normal distribution of window diameters:

$$f(d_p) = \frac{1}{\sigma_G \sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{d_p - \mu}{\sigma_G}\right)^2\right) \quad (1)$$

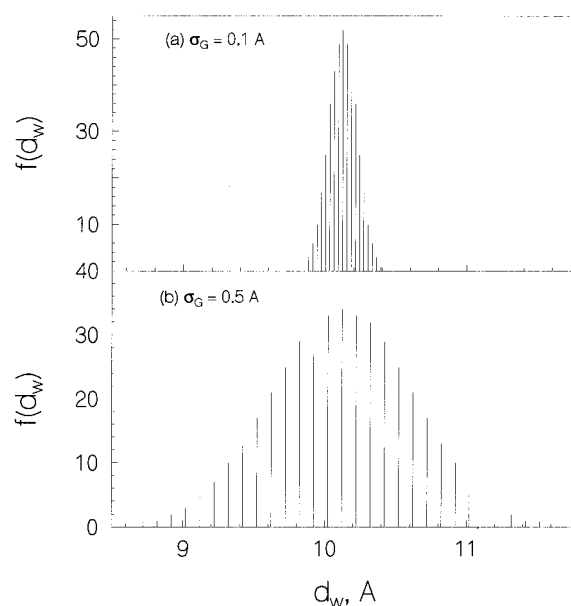


Figure 2. Distribution of window diameters (a) when $\sigma_G = 0.1$ Å and (b) when $\sigma_G = 0.5$ Å.

TABLE 1: Self-Interaction Potential Parameters for Different Zeolite Atoms

type	σ , Å	ϵ , kJ/mol
O–O	2.5447	1.289134
Na–Na	3.369378	0.0392347
Ca–Ca	3.35	9.545046

where $\mu = 10.11422$ Å the diameter of the 12-ring window in crystalline faujasite with Si/Al = 3.0 and σ_G is the half-width at half-maximum. d_p is the diameter of the 12-ring window. Three different values were chosen for σ_G , corresponding to increasing disorder: (i) 0, which corresponds simply to the perfectly crystalline zeolite Y structure, (ii) 0.1 Å, a rather narrow width to the Gaussian, and finally, (iii) 0.5 Å, a rather broad width to the Gaussian. Figure 2 shows these distributions. The size of the simulation cell is $3 \times 3 \times 3$ unit cells, leading to a total of 27 crystallographic cells and 216 α -cages. The distribution function shown in Figure 2, therefore, adds up to 432, which is the total number of 12-ring windows in the system. The diameter d_p of a given window was selected randomly from the distribution and the 12 oxygen atoms of the window were displaced approximately either toward or away from the window center by an amount $|\mu - d_p|/2$, so as to achieve the desired diameter d_p . Once most of the 432 windows were assigned the diameter from the distribution, only a few choices would be left and these were chosen for the remaining windows.

The interaction among the guests as well as between the guest and the zeolite atoms were chosen to be of the (6-12) Lennard-Jones form, as discussed in ref 1. The potential parameters originally proposed by Kiselev and Du¹² and employed in earlier studies^{1,2} were employed here. These are listed in Table 1. The size of the guest or sorbate was varied between 2.67 and 6.80 Å as the earlier work of Yashonath and Santikary² suggests that this range would span both the linear and anomalous regimes discussed earlier.

Molecular dynamics simulations in the microcanonical ensemble were carried out using the velocity Verlet algorithm at a loading of 1 guest per α -cage, which corresponds to simulations on a system with 216 guests. All simulations were carried out with a time step of 30 fs, a guest mass of 131 amu, and a cutoff radius of 12 Å. Runs were equilibrated for a period of

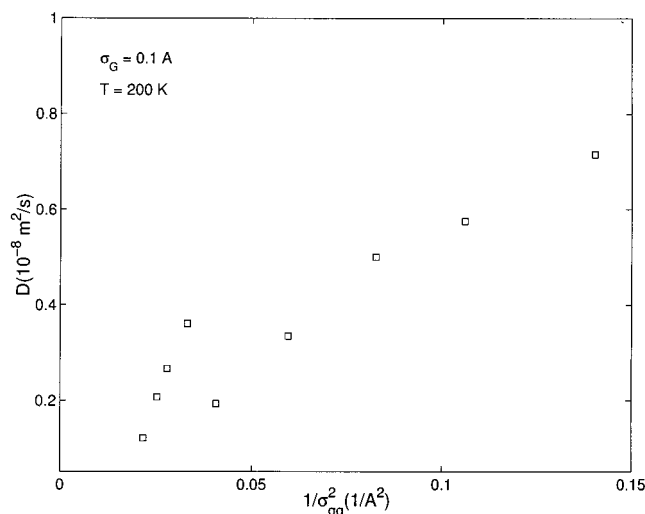


Figure 3. D vs $1/\sigma_{gg}^2$ plot in the case of $\sigma_G = 0.1$ Å, at $T = 200$ K.

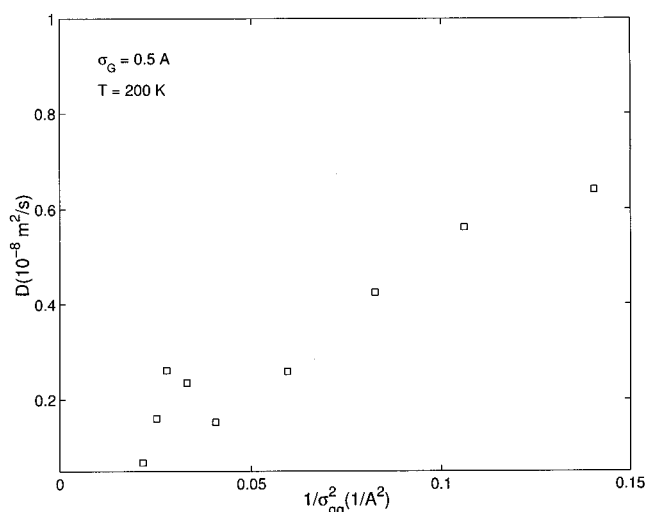


Figure 4. D vs $1/\sigma_{gg}^2$ plot in the case of $\sigma_G = 0.5$ Å, at $T = 200$ K.

0.6 ns and properties accumulated over a duration of 2.1 ns. The ϵ_{gg} is 221 K, corresponding to xenon.

III. Results and Discussion

A. $D - 1/\sigma_{gg}^2$ Behavior and Disorder in the Window Diameter. Self-diffusivity, D , is plotted against $1/\sigma_{gg}^2$ in Figure 3, for $\sigma_G = 0.1$ Å. This may be compared with Figure 1, which shows the D vs $1/\sigma_{gg}^2$ curve for $\sigma_G = 0.0$ Å. Two differences may be noted: (i) there is a small decrease in the intensity of the anomalous peak at large σ and (ii) the D vs $1/\sigma_{gg}^2$ in the “linear regime” is no longer a straight line, which suggests a breakdown of the linear proportionality that exists between self-diffusivity and the reciprocal of square of the sorbate-sorbate Lennard-Jones interaction parameter σ_{gg} . Figure 4 shows the $D - 1/\sigma_{gg}^2$ plot for $\sigma_G = 0.5$ Å. The anomalous intensity has further decreased to about 60% of its value found when $\sigma_G = 0.0$ Å. The breakdown of the linear proportionality between D and $1/\sigma_{gg}^2$ persists.

To obtain an insight into the diffusion—especially diffusion past the 12-ring window—we have looked at the variation of the energy and the frequency of crossover from one α -cage to another. Figure 5 shows a plot of the total potential energy U , as a function of the distance, d , from the plane of the 12-ring window through which the particle has to pass to migrate to a neighboring cage. The curve was obtained by first making a

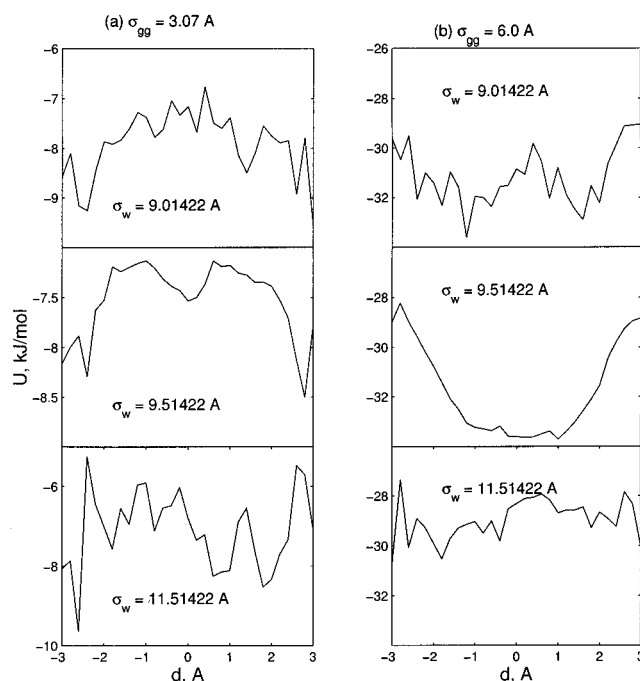


Figure 5. Total potential energy, U , vs the distance, d , of the particle from the plane of the window for (a) $\sigma_{gg} = 3.07$ Å for three different window diameters, viz., 9.01, 9.514, and 11.514 Å. (b) The same for $\sigma_{gg} = 6.0$ Å.

list of all cage-to-cage crossover events and the time at which the crossover takes place. Then we looked at the trajectory a few picoseconds before and after the crossover event. The value of d and the corresponding value of U were obtained by averaging over all these trajectories. The curves $U(d)$ are shown for two different values of σ_{gg} : (a) 3.07 Å (from the “linear regime”) and (b) 6.0 Å (from anomalous regime) at three different (small, medium and large) values of σ_w : (i) 9.014 Å, (ii) 9.514 Å, and (iii) 11.514 Å. The curves for $\sigma_{gg} = 3.07$ Å, which lie in the linear regime, always show no minima but rather exhibit a maximum in U at $d = 0$, i.e., when the particle is in the plane of the 12-ring window. This is when the particle is just passing through the 12-ring window. In contrast to this, when $\sigma_{gg} = 6.0$ Å, the $U(d)$ curve shows a minimum at $d = 0$ for all the three different values of σ_w . However, the minimum is most pronounced for $\sigma_w = 9.514$ Å. This behavior is similar to that observed for the case $\sigma_G = 0.0$ Å earlier.²

$U(d)$ shows a much larger barrier (or minima) for $\sigma_{gg} = 3.07$ Å (6.0 Å) for the two extreme dimensions of window diameters, viz., $\sigma_w = 9.014$ and 11.514 Å. In comparison to these, the barrier (or minima) is much smaller in magnitude for $\sigma_w = 9.514$ Å. The levitation ratio, γ , is 0.699 (1.064 for 6.0 Å), 0.662 (1.008), and 0.547 (0.833) for $\sigma_w = 9.012$, 9.514, and 11.514 Å. Thus, as γ approaches unity, the difference in U between its values within the α -cage and at the window decreases. Here γ is the levitation parameter given by

$$\gamma = \frac{2.2^{1/6} \sigma_{sz}}{\sigma_w} \quad (2)$$

where σ_{sz} is the Lennard-Jones interaction parameter between the sorbate and the oxygen of the zeolite. σ_w is the window diameter defined as the distance between the two diagonally located oxygens lying in the plane of the window. The observed variation in the barrier height obtained from $U(d)$ when the particle is passing through the window has been seen earlier¹⁴

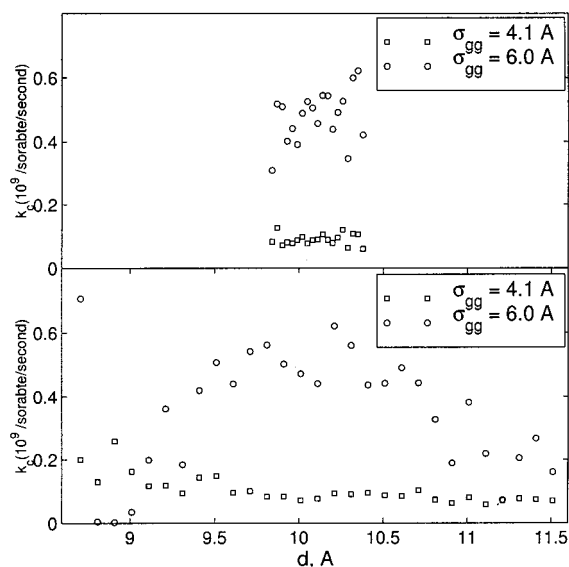


Figure 6. Rate of intercage cross over, k_c , in units of per guest particle per second vs d for (a) $\sigma_G = 0.1$ Å and (b) $\sigma_G = 0.5$ Å at 200 K.

TABLE 2: Self-Diffusivities of Particles with $\sigma_{gg} = 4.1$ and 6.0 Å for Three Different Window Dimensions at Different Temperatures

temp (K)	$D, (\times 10^8 \text{ m}^2/\text{s})$			
	$\sigma_w = 8.714$ Å		$\sigma_w = 11.514$ Å	
	$\sigma_{gg} = 4.10$ Å	$\sigma_{gg} = 6.0$ Å	$\sigma_{gg} = 4.10$ Å	$\sigma_{gg} = 6.0$ Å
100	0.0169	0.0076	0.0082	0.0488
200	0.2034	0.0242	0.3517	0.3979
300	0.5003	0.0380	1.0645	0.4133

and relates to the better coordination of the sorbate near the window when γ approaches unity.

Rate of intercage migration, k_c , defined as the number of cage-to-cage crossovers per unit time per particle can be calculated by assigning every particle at any given molecular dynamics time step to a particular cage. A particle is assigned to the cage whose center is nearest to the particle. Variation of k_c with σ_w is shown in Figure 6, for (a) $\sigma_G = 0.1$ and (b) 0.5 Å, for $\sigma_{gg} = 4.1$ and 6.0 Å. It is seen that both 4.1 and 6.0 Å sized sorbates diffuse with uniform frequency through the windows of various dimensions in the case of $\sigma_G = 0.1$ Å. This is not surprising since the variation in σ_w is rather narrow when $\sigma_G = 0.1$ Å.

In the case of $\sigma_G = 0.5$ Å the window dimensions vary over a significant range. k_c still shows a nearly uniform variation with d for $\sigma_{gg} = 4.1$ Å. This is because for the particle of this size, γ is far from unity for all sizes of σ_w . This is not the case for $\sigma_{gg} = 6.0$ Å, which shows that k_c is a maximum for medium dimensions of σ_w and smaller at extremes: large as well as small values of σ_w .

B. Activation Energies. Unlike the barrier in the potential energy, activation energy is a phenomenological quantity defined by the Arrhenius expression.^{15,16} The activation energy for two extreme values of σ_w : (i) 8.714 Å and (ii) 11.514 Å for $\sigma_{gg} = 4.1$ and 6.0 Å have been obtained by us by carrying out simulations at several temperatures. The values of D are listed to Table 2. This was obtained by carrying out four independent MD runs in which all windows were uniformly 8.714 Å (in two runs with $\sigma_{gg} = 4.1$ and 6.0 Å) and 11.514 (in two runs with $\sigma_{gg} = 4.1$ and 6.0 Å). These window dimensions are the smallest and largest found in $\sigma_G = 0.5$ Å. The activation energies are listed in Table 3. It is seen that the activation energy is always lower for $\sigma_{gg} = 6.0$ Å, usually by a factor of 2.

TABLE 3: Activation Energies of Particles with $\sigma_{gg} = 4.1$ and 6.0 Å for Three Different Window Dimensions

$\sigma_{gg}, \text{Å}$	$E_a, \text{kJ/mol}$	
	$\sigma_w = 8.714$ Å	$\sigma_w = 11.514$ Å
4.10	4.204	6.103
6.00	1.988	2.856 13

IV. Conclusions

Anomalous diffusion persists even when the window dimensions, which is usually the bottleneck for diffusion, interconnecting voids are not unique but vary over a range of values. In other words, even when there is a degree of disorder in the pore dimensions, the anomalous diffusion persists provided this range is not too wide. This is certainly true for a normal distribution of pore dimensions. It is to be seen whether for other distributions of pore dimensions the levitation effect will persist. Two significant changes are observed with an increase in disorder: (i) a decrease in the intensity of the anomalous peak and (ii) a breakdown of a linear relationship between the self-diffusivity and $1/\sigma_{gg}^2$ in the nonanomalous regime.

These results may be compared with the effect of an increase in temperature on the $D - 1/\sigma_{gg}^2$ curve.¹³ An increase in temperature resulted in a decrease in the intensity of the anomalous peak, though not to a breakdown of the linear proportionality between D and $1/\sigma_{gg}^2$. Thus, in a limited sense both an increase in temperature and the disorder in the pore dimensions have similar effects of decreasing the intensity of the anomalous peak. An increase in the temperature leads to an increase in disorder due to the increased randomization of the velocities. In the present study, the randomization is of the window dimensions. The latter leads not only to a decrease in the intensity of the anomalous peak but also to a nonlinear relationship between D and $1/\sigma_{gg}^2$.

When $\sigma_G = 0.5$ Å, the range of window diameter extends from 8.714 to 11.514 Å. This range of nearly 3 Å is quite significant on a molecular length scale. If the σ_w^{opt} is the optimum window diameter corresponding to the peak in D and therefore to a value close to unity for the levitation ratio, then it seems that the anomalous peak intensity remains significant (at worst 60% of the original intensity) even when σ_w varies between $\sigma_w^{\text{opt}} \pm 1.5$ Å. This seems to be true at least for a Gaussian pore distribution. This suggests that even in a noncrystalline porous solid with a rather large (± 1.5 Å) variation of the pore diameters, one can expect the levitation effect. The present study suggests that a reasonably wide range of window dimensions (± 1.5 Å) are acceptable. If one wants to use anomalous diffusion for separation of mixtures within a noncrystalline porous host, then the important question would be, what is the largest value of σ_G that would still exhibit anomalous diffusion? Though we cannot answer this, it is evident that at least a value of $\sigma_G = 0.5$ Å would be acceptable.

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