



Collective diffusion coefficient in limited channel: two methods for fluid particles

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Abstract. Molecular dynamics and Monte Carlo methods are common measurements to study the diffusion coefficients of the fluid particles under restricted conditions. Here, the collective diffusion coefficient will be obtained through two methods: the one is Fick's first law (direct mode), and the other is the relationship between collective diffusion coefficient and self-diffusion coefficient (indirect mode). A comparison between two methods is also discussed. The ways of calculation, which are applied for the self-diffusion coefficient and collective diffusion coefficient, are helpful for studying transport characteristics of various molecules in defined space.

1 Introduction

Diffusion coefficient can be divided into collective diffusion coefficient (CDC) and self-diffusion coefficient (SDC), which are important characteristic parameters of fluid particles [1–3]. The current research results of diffusion coefficient have a great difference on the range of $10^{-9} - 10^{-7} \text{ m}^2/\text{s}$ [4–9]. Due to the different models and the difficulty of experimental research, there is still no unified standard for the determination and calculation of the diffusion coefficient, especially the collective diffusion coefficient.

Two methods including the indirect way of self-diffusion coefficient and direct way of Fick's first law can obtain the collective diffusion coefficient. The first method is mainly used when Fick's law cannot be used to directly calculate the collective diffusion coefficient [10]. For example, in the case that the evolution of all particles cannot be traced directly, we can only obtain the self-diffusion coefficient first, and then use the relationship between the SDC and the CDC to calculate the collective diffusion coefficient indirectly [11–14]. The same is true for models with no chemical potential difference (including difference in concentration or temperature) [8, 15]. Up to now, most of the existing studies use the formula of free self-diffusion to calculate the self-diffusion coefficient [7–9, 16, 17]. However, the particles always move in a limited space, which means that the diffusion of particles should be restricted rather than free, then it is necessary to study the rationality of this approximate treatment.

In this paper, we first obtain the collective diffusion coefficient by two methods, then compare the results of

the two methods, and finally, we deeply discuss the calculation method of diffusion coefficient under restricted environment.

2 Models and methods

2.1 The model and method of collective diffusion coefficient are obtained from self-diffusion coefficient

Self-diffusion refers to the diffusion caused by the Brownian motion of a molecule, the self-diffusion coefficient is usually obtained by Einstein–Smoluchowski relations. Collective diffusion refers to the diffusion behavior caused by a concentration gradient, whose diffusivity is determined by the Fick's law. Generally, the self-diffusion coefficient and the collective diffusion coefficient satisfy certain mathematical relations as shown in Eq. (3).

Figure 1 shows the model to determine the collective diffusion coefficient by studying self-diffusion. Figure 1a shows the cross-section and the normal section of carbon or silicon nanotubes. The green particles represent the diffusion particles, and the left and right sides of the cross-section add reflection boundaries to form a closed space. Figure 1b shows a cross-section of a sphere with radius, r , with soft walls at the boundary and green particles representing diffuse particles.

Molecular dynamics was used to simulate the motion of particles, He, and the van der Waals interaction between particles is described by Lennard-Jones model [18].

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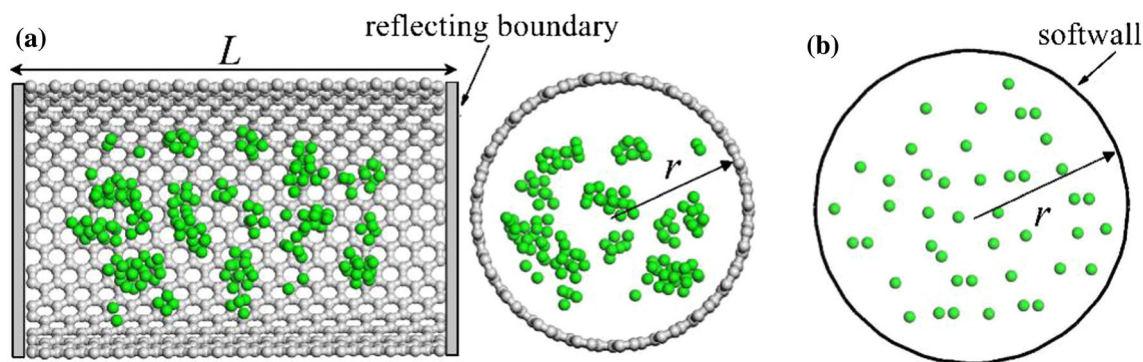
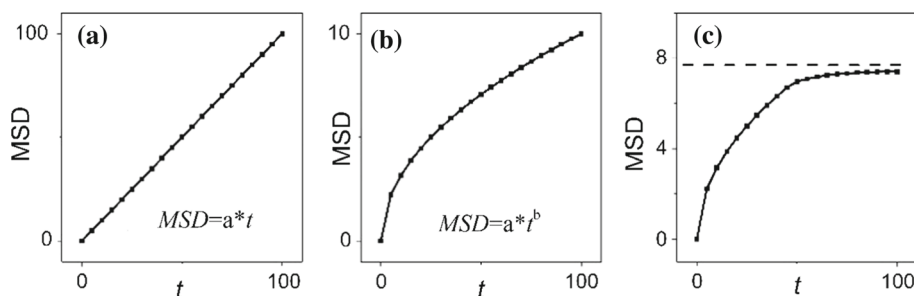


Fig. 1 Schematic to study the self-diffusion coefficient

Fig. 2 Mean square displacements in different self-diffusion modes: **a** free diffusion; **b** blocked diffusion; **c** restricted diffusion



Self-diffusion can be divided into three types: free diffusion, blocked diffusion and restricted diffusion. Particles do not meet the obstacle in the process of diffusion when they move in infinite space, which called free diffusion. Particles will encounter resistance other than particles in the process of diffusion, but the diffusion space is infinite, which called hindered diffusion. Under restricted diffusion, the particle self-diffuses in a finite space. Figure 2 shows the relationship between mean square displacement (MSD) and diffusion time under these three self-diffusion conditions.

The MSD and the self-diffusion can be expressed as [19]

$$\text{MSD} = \langle (r_n(t) - r_n(0))^2 \rangle = \frac{1}{N} \sum_{n=1}^N (r_n(t) - r_n(0))^2, \quad (1)$$

where r is the displacement, N the number of particles, t time of diffusion, and $t = 0$ original time of motion, respectively.

The self-diffusion coefficient can be written as [14, 20]

$$D_s = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\partial \text{MSD}}{\partial t}, \quad (2)$$

where d denotes the number of dimension. D_s corresponds to the slope of the curve in Fig. 2. The figure shows that for free diffusion, the slope is fixed which leads to the constant diffusion coefficient while the diffusion coefficients of hindered and restricted diffusion vary with time, so choosing the right time point

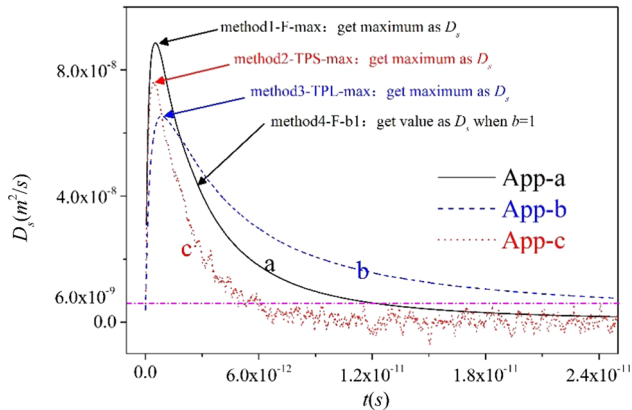
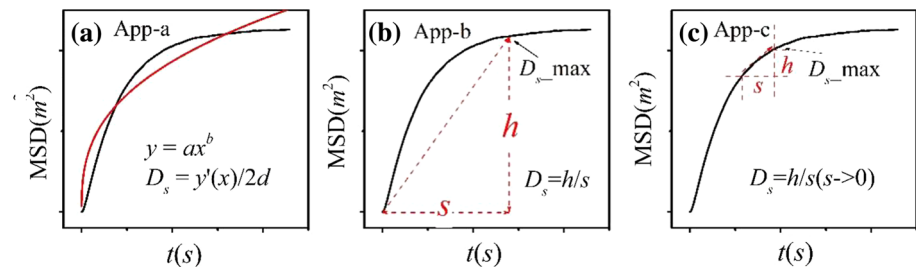
becomes a matter of concern in study. The conditions of researches belong mainly to restricted diffusion because most research environments are limited in space actually.

Figure 2c and Eq. (2) imply that the self-diffusion coefficient of restricted diffusion cannot be solved directly, so the diffusion should be approximated.

The first approach is to approximate the restricted diffusion as the blocked diffusion. Figure 2c shows the nonlinear fitting (the fitting equation: $\text{MSD} = a \cdot t^b$) about the relationship between the self-diffusion coefficient and the sampling time (D_s vs t). For convenience, the approximate processing is called approximation-a (App-a), which requires a large amount of computation.

The second approximation is to approximate restricted diffusion as free diffusion by selecting two points on Fig. 2c to obtain the slope of the self-diffusion coefficient, which requires less work of computation. It can be subdivided into two methods depending on the selected points. One is to select the fixed point (0, 0) as the original point, select (t, MSD) as another point, and obtain the diffusion coefficient at time t , which is named as approximation-b (App-b). The second is to select two points $(t - \Delta t, \text{MSD})$ and (t, MSD) to obtain the diffusion coefficient of time t , where Δt represents a short period of time, which is named as approximation-c (App-c). Figure 3 displays the schematic diagram of the three approximations.

According to the mechanism of the three approximate processing methods, it is also known that in the case of rather small limited space, the restricted diffusion is very similar to the blocked diffusion, but not

Fig. 3 Three approximate diagrams for mean square displacement**Fig. 4** D_s vs t lines obtained by three approximate treatments and methods for obtaining final D_s . Parameter: self-diffusion environment is CNT; length is 2 nm; chirality is (16,16); apply reflective borders on both sides to form a limited space

consistent with the free diffusion, so it is more appropriate to choose App-a. However, in the case of large restricted space, restricted diffusion will be close to free diffusion, so it is convenient to choose App-b and c. In conclusion, since it is difficult to determine the standard of the size of the restricted space, App-a is more general in terms of algorithm, and it is more recommended to approximate the restricted diffusion in this way.

The relation between the self-diffusion coefficient and the sampling time can be obtained through three approximate processing methods of app-a, b and c. The three lines in Fig. 4 are obtained using three approximate processing methods of App-a, b and c. Since D_s is related to the sampling time t , the final self-diffusion coefficient should be determined by selecting the appropriate sampling time as the additional method.

In Fig. 4, four selection methods are proposed of which names are shown in Table 1.

The last of the four methods (method4) is to select the diffusion coefficient corresponding to the fitting parameter $b = 1$ as D_s . When $b = 1$, it means that it is in a state of free diffusion at that moment, while the method4-F-b1 selection method itself adopts the approximate treatment of App-a, so the approximate treatment of restricted diffusion is restricted diffusion. Selecting the corresponding point $b = 1$ is equivalent to approximating the restricted diffusion as free diffusion and blocked diffusion. Therefore, algorithmically, the method4-F-b1 should be recommended first.

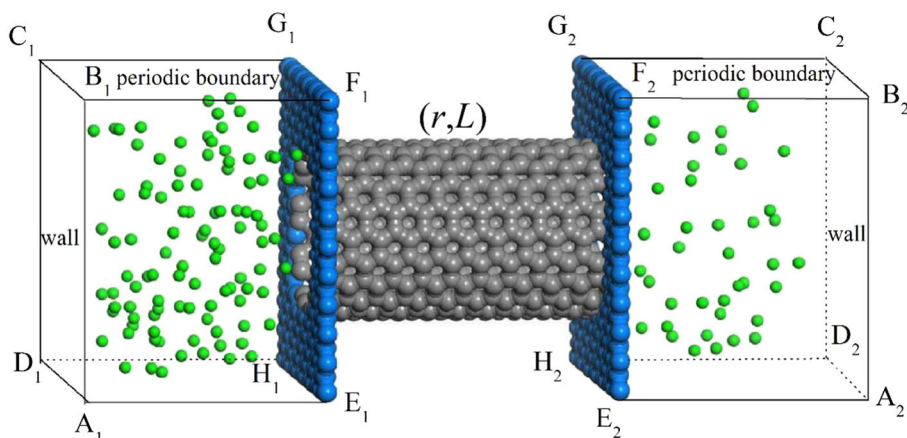
Table 1 Method for selecting sampling time point (to obtain the final self-diffusion coefficient)

Methods	Annotations
Method1-F-max	Obtain D_{s_t} curve by approximation-a, select the maximum value as D_s
Method2-TPS-max	Obtain D_{s_t} curve by approximation-c, select the maximum value as D_s
Method3-TPL-max	Obtain D_{s_t} curve by approximation-b, select the maximum value as D_s
Method4-F-b1	Obtain D_{s_t} curve by approximation-a, the corresponding diffusion coefficient when the fitting parameter $b = 1$ is selected as D_s

The first three of the four methods (method1 to method3) select the maximum value as D_s . This is because in the limited space, the particle is in the state of self-diffusion all the time, but when the relation between MSD and time t is obtained, a fixed original time point t_0 must be selected, which leads to the fact that in the MSD vs t line, MSD must approach to a stable value. At this point, the slope of the line is close to 0, but the particles are still in the state of self-diffusion. Therefore, the MSD vs t line cannot describe the restricted diffusion very well, and the MSD vs t line can only describe the restricted diffusion within a limited period of time. Therefore, it can be considered that the maximum value in the D_s vs t line can represent the self-diffusion coefficient of particles to a certain extent.

In addition, Fig. 4 shows that as time increases, D_s eventually approaches a small value or even approaches 0. This is precisely because the MSD vs t line is not a good description of restricted diffusion in fact, and can only be used to describe restricted diffusion within a limited period of time. However, in some studies, the restricted diffusion may be simply regarded as free diffusion, and it is necessary to choose a long diffusion time in the free diffusion when calculating the diffusion coefficient, which leads to the case that the diffusion coefficient is very small. Figure 4 also shows that the maximum value and the approach value under a long sampling time can be more than one order of magnitude different, so it can be considered that some studies

Fig. 5 Diagram of collective diffusion for directly studying



may inadvertently select the value near the maximum value as D_s , resulting in a very large diffusion coefficient. While the highest value in Fig. 4 orders of magnitude is small, it cannot explain why diffusion coefficient appears to be very big (up to $10^{-5} \text{ m}^2/\text{s}$) [7, 8], but Fig. 4 shows that the selection of D_s in different ways can have more than one order of magnitude of the differences, which also can partly explain the current collective diffusion coefficient results by two orders of magnitude.

The self-diffusion coefficient is finally obtained by the above four selection methods. Since the final requirement is to obtain the collective diffusion coefficient, the relationship between the collective diffusion coefficient and the self-expansion coefficient should be used. The relationship can be as follows [11–14]:

$$D_t(c) = D_s(c) \cdot \left(\frac{d \ln p}{d \ln c} \right), \quad (3)$$

where $D_t(c)$ is the collective diffusion coefficient, $D_s(c)$ the self-diffusion coefficient, c is the concentration, and p is the effective pressure of the actual gas, which is solved by the equation of state.

2.2 The model and method of collective diffusion coefficient are obtained directly from Fick's law

Since it is difficult to obtain the collective diffusion coefficient directly in the experiment, the self-diffusion coefficient is usually obtained first and then the collective diffusion coefficient is calculated by Eq. (3). In the simulations, the collective diffusion coefficient can be obtained directly by Fick's first law. In 1855, Adolf Fick derived Fick's law, which can be expressed as [12]

$$J = D \frac{dc}{dL}, \quad (4)$$

where J is the diffusion flux that refers to the mass per unit area per unit time, D the diffusion coefficient, c the concentration (assuming an ideal mixture), and L the length, respectively.

Figure 5 shows the model for studying collective diffusion directly. The left and right boxes represent the left and right libraries. The size and shape of the boxes are both $A_1 B_1 \times A_1 D_1 \times A_1 E_1 = 4 \times 4 \times 4 \text{ nm}$, where $A_1 B_1 C_1 D_1$ is the wall, $E_1 F_1 G_1 H_1$ is the wall made up of Si atoms (blue part), and the remaining four faces are the periodic boundary. The gray part in the middle is the silicon nanotube channel, radius r , length L .

Molecular dynamics is used to calculate the motion of particles and the Monte Carlo method is used to control the number of particles in the left and right baths [21, 22]. The temperature is controlled using Langevin random heat baths [23, 24].

3 Results and analyses

3.1 Collective diffusion coefficient obtained from the self-diffusion coefficient in the restricted space

Using the four selection methods provided in Table 1 (or Fig. 4), the relation between the self-diffusion coefficient and the concentration can be obtained, as shown in Fig. 6. The collective diffusion coefficient can be calculated by Eq. (3), as shown in Fig. 6.

Figure 6 shows that the diffusion coefficients obtained by the four selection methods do not differ greatly, but there are still differences between them, among which the diffusion coefficient obtained by method1-F-max is the largest, and the self-diffusion coefficient obtained by method4-F-b1 is the smallest.

According to the analysis in the model and methods, from the point of view of algorithm, method4-F-b1 is the preferred selection method in recommendation, so it is necessary to prove whether method4-F-b1 is the most suitable algorithm.

Figure 7 illustrates the transition from restricted to free diffusion, where the dotted line is the diffusion coefficient of free diffusion at different temperatures (also calculated by simulation), the solid line represents the restricted diffusion. The model introduced is the spherical soft wall model in Fig. 1b and the x -coordinate r is

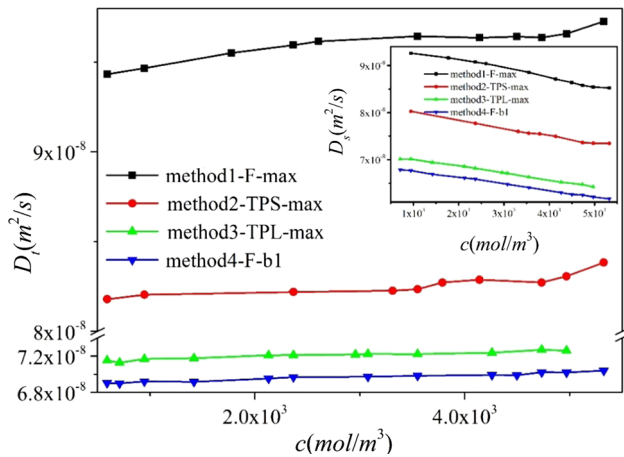


Fig. 6 Collective diffusion coefficients from the self-diffusion coefficients (inset) using four selection methods (larger image). Parameter: the self-diffusion environment is SiNT, the length is $L = 4$ nm, and the radius is $r = 2$ nm. Apply reflective borders on both sides to form a limited space

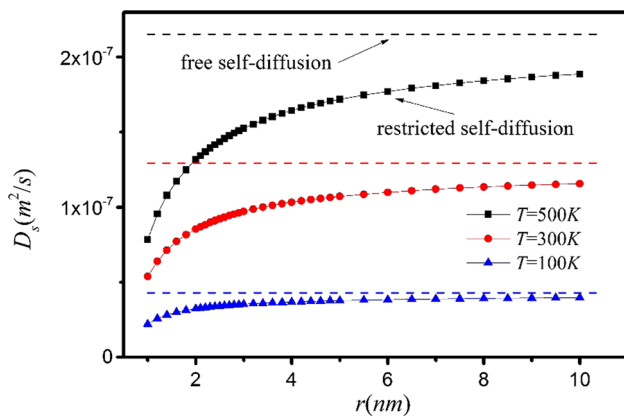


Fig. 7 From restricted diffusion to free diffusion. Model parameters: using the spherical soft wall model of Fig. 1b, the self-diffusion coefficient D_s was obtained using method4-F-b1

the radius of the spherical model. The bigger r is, the bigger the diffusion space is, and then the closer it is to free diffusion.

As shown in Fig. 7, with the increase of r , the restricted diffusion gradually transitions to free diffusion at lower the temperature, which is in good agreement with the result of free diffusion. The results also show that method4-F-b1 is an appropriate method. As shown in Fig. 6, the diffusion coefficient obtained by other methods is larger than that obtained method4-F-b1, which also indicates that the diffusion coefficient will be larger if other methods are introduced.

In some specific cases, such as in experiments, it is often difficult to obtain the collective diffusion coefficient directly, and the collective diffusion coefficient can only be calculated by obtaining the self-diffusion coefficient first. In this case, it is recommended that

method4-F-b1 can be used to obtain the self-diffusion coefficient.

Here, we have to point out that in our simulations, the largest size of the system is only 10 nm. As shown in Fig. 7, in the range of 8–10 nm, the diffusion coefficient tends to a stable value. That means the diffusion coefficient have approached the thermodynamic limit. For low temperature, the diffusion coefficient is almost equal to the value of free self-diffusion. Therefore, the system size used in this work provides enough space for the relaxation of particles.

3.2 Collective diffusion coefficient obtained from Fick's law

In addition to the indirect calculation of the collective diffusion coefficient by self-diffusion, the collective diffusion coefficient can be obtained directly using Fick's law in some models as shown in Fig. 5.

Figure 8 shows that the collective diffusion coefficient can be obtained in both ways, where the solid line of the black square is the result of collective diffusion indirectly obtained by self-diffusion (the selection method of method4-F-b1 is introduced). The model is shown in Fig. 1a, and the parameter is: SiNT of which the length is $L = 4$ nm, the radius $r = 2$ nm, and the reflection boundary is applied to both sides to form a finite space. The solid line of the purple triangle is the result of the direct calculation of the collective diffusion coefficient by Fick's law. The model is shown in Fig. 5 and the parameters of the channel are: SiNT of which the length is $L = 4$ nm, and the radius is $r = 2$ nm.

Figure 8 presents that there is little difference in the collective diffusion coefficient obtained by the two methods, which indicates that both methods are desirable and both methods have advantages as well as disadvantages.

For the indirect method, the advantage of solving the CDC indirectly through self-diffusion is that it can solve some cases where the CDC cannot be solved

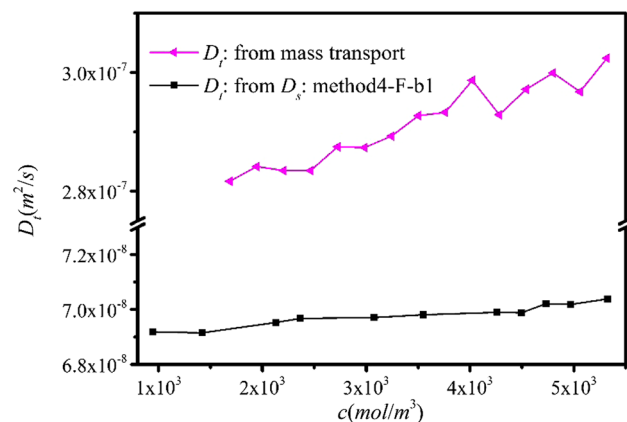


Fig. 8 A comparison of the collective diffusion coefficient obtained directly through indirect diffusion (method4-F-b1) and through Fick's law (mass transport)

directly. The disadvantage is that the calculation process is rather tedious, the type of self-diffusion needs to be considered, the approximate processing method, and the sampling time has a great impact on the results, which leads to a huge error in the calculation of D_s , but if the normal diffusion is used as the benchmark, the result is closer to the real value.

For the direct method, the advantage of calculating the CDC directly by Fick's law is that it is more reasonable, easier to operate, and more accurate. It is suitable for obtaining the CDC when the concentration difference is very small whereas the disadvantage is that the size effect is obvious, the calculation is complex, and in practice if the concentration difference is too small, the mass flow cannot be formed large enough, which also leads to a certain error between the simulation result and the theoretical value.

4 Conclusions

In this paper, the accessibility of collective diffusion coefficient calculated by indirect way of self-diffusion and direct way of Fick's law is studied by the mean of molecular dynamics and Monte Carlo methods. Studying the calculation of collective diffusion coefficient of molecules under restricted space is the main point here. The following results were obtained:

First, although the restricted self-diffusion coefficient was obtained by mean square displacement, the self-diffusion coefficient would be a function of the sampling time on account of the incompatibility of the method by itself. As the sampling time increases, the self-diffusion coefficient first increases, then decreases, and finally approaches zero, which lead to an order of magnitude difference in the diffusion coefficient. From this point of view, a appropriate sampling time should be chosen to obtain the self-diffusion coefficient. We suggest method4-F-b1 to be the most appropriate method which is one of the four methods of obtaining self-diffusion coefficient we provided. Restricted diffusion of self-diffusion coefficient, a function of time by the mean of the nonlinear fitting, is approximated to hindered diffusion in method4-F-b1 and it is fixed as the final self-diffusion by selection of the time point of the particle in the state of free diffusion.

Second, by comparing the indirect and direct methods to obtain the collective diffusion coefficient, the results show that the two methods are accessible and each has their advantages and disadvantages. The advantage of calculating the collective diffusion coefficient indirectly by self-diffusion is that some models which cannot calculate the collective diffusion directly can be applied, while the disadvantage is that there are many steps and complication in the process as well as the strong dependence on the sampling time and large errors on account of the approximate process. The advantages of direct calculation by Fick's law are more reasonable, easy to operate and high accuracy, while the disadvantage is that the size effect is obvious and the

calculation is complicated. In the experiment operation, the appropriate method should be selected according to the actual situation.

Third, the results obtained from this paper account for the difference of two orders of magnitude between self-diffusion and collective diffusion coefficients in the groups of different research and provide an available way to study other transport characteristics of fluid molecules.

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Author contributions

ZWR designed the research, CPR performed the research, and ZMP wrote the manuscript.

Data availability statement This manuscript has no associated data, or the data will not be deposited. [Authors comment: Our results are calculated by our own program and are easily repeatable. Therefore, it is not necessary to store all the original data.]

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