On the characterization of nanoporous materials by means of empirical and intrinsic transport coefficients

Till Frank*

Institute for Theoretical Physics, University of Muenster, Wilhelm-Klemm-Str. 9, 48149 Muenster, Germany

Received 12 January 2005; revised 8 March 2005; accepted 8 March 2005
Available online 20 June 2005

Abstract

Nanoporous materials need to be classified and characterized both for scientific research and applications in industrial production and environmental protection. Nanoporous materials with simple geometries (e.g. channel pores, slit pores) can be characterized by means of transport coefficients such as diffusion and viscosity coefficients of the fluid and gas flows through these materials. To this end, empirical transport coefficients defined by the Einstein relation and the Green–Kubo formula are frequently used. In the present study, it will be shown that the applicability of empirical transport coefficients is limited because of the confinement of fluid molecules in nanopores and the direct and indirect molecule–molecule interactions. It will be advocated that transport properties of nanoporous materials are better described by transport coefficients different from empirical transport coefficients such as intrinsic transport coefficient defined by Brownian dynamics models.

Keywords: Nanoporous materials; Transport coefficients; Data analysis; Drift and diffusion estimates

1. Introduction

Porous materials are frequently used in chemical processes and petroleum processing as catalysts and adsorbents. They came as naturally nanoporous materials such as zeolites and as synthetic ones. The transport coefficients of fluid flows through these materials are of particular interest for applications. An in-depth understanding of transport processes in nanoporous materials is therefore crucial for the design of many processes in petroleum industry and environmental protection. Two methods are often used to determine transport coefficients such as diffusion coefficients and viscosities. These two methods are related to the Einstein relation, on the one hand, and the Green–Kubo relation, on the other hand. The Einstein relation states that the mean-square displacement (MSD) of fluid molecules displacements increases in the asymptotic limit linear with time with the diffusion tensor as a proportional factor. Accordingly, the MSD components divided by time give us the diffusion tensor components $D^E$ in the long time limit

$$D^E = \lim_{t \to \infty} \frac{1}{6t} \langle \Delta r^2(t) \rangle,$$

where $\Delta r(t) = r(t) - r(0)$ describes the displacement of molecules and the MSD as a function of time is given by $\langle \Delta r^2(t) \rangle$. Likewise, the Green–Kubo relation states that the viscosity of a fluid is given by the time integral over the autocorrelation function of the momentum flux. We will refer to transport coefficients defined by the Einstein relation and the Green–Kubo relation as empirical transport coefficient. Taking a theoretical point of view both methods apply only for fluids with non-interacting fluid particles/molecules and unrestricted domains. If we wish to determine transport coefficients for fluids that are confined to cavities and/or exhibit particle–particle interactions neither the Einstein relation nor the Kubo relation [1] are valid approaches. In order to cope with this problem, we suggest to exploit relationships from the theory of Brownian dynamics (BD) in order to define and estimate transport coefficients. We will refer to transport coefficients related to BD models as intrinsic transport coefficients. For example, the theory of BD states that diffusion coefficients are given...
by so-called second order Kramers–Moyal coefficients. These coefficients are uniquely defined and can be applied to all kinds of systems including systems that are confined to bounded domains and consist of interacting subsystems [2]. Accordingly, for simple flows through nanoporous materials the BD diffusion tensor, \( D^I \), is given by the MSD components divided by time in the short time limit:

\[
D^I = \lim_{t \to 0} \frac{1}{6t} \langle \Delta r^2(t) \rangle.
\]

That is, whereas the empirical diffusion coefficient involves the long time behavior, the intrinsic diffusion coefficient involves the short time behavior. Intrinsic transport coefficient have been successfully applied in different disciplines (see Table 1).

### 2. Model and methods

In order to illustrate the difference between empirical and intrinsic transport coefficients, the diffusion of fluid molecules in a rectangular channel is considered (length \( L \), width and height \( d \), with \( L \) much larger than \( d \)). The principle axis of the channel is in the \( x \) direction and the flow is confined in the \( y \) and \( z \) directions by the channel walls, see Fig. 1. The fluid particles are assumed to satisfy the free diffusion equation unless they hit the walls. Neglecting the atomistic structure of the channel walls, we require that completely reflective boundary conditions hold in case of contact with the walls. In contrast, we assume that the particle motion is not confined along the \( x \) direction.

#### 3. Results and discussion

Let \( D \) denote the diffusion tensor of the free diffusion equation with components \( D_x, D_y, \) and \( D_z \). Likewise, let \( D^E \) and \( D^I \) denote the empirical and intrinsic diffusion tensors defined above with components \( D^E_x, D^E_y, D^E_z; \) and \( D^I_x, D^I_y, D^I_z \), respectively. The MSD in \( y \) and \( z \) directions increases monotonically as a function of time and converges to a saturation value due to the confinement of the fluid molecules. We have

\[
\text{MSD}(t) = C(1 - \exp(-2t/C)),
\]

where \( C \) is a constant [11]. Consequently, the components \( D^E_x \) and \( D^E_y \) become functions of time and decrease to zero for very large observation times, see Fig. 2.

In addition, one can then show that \( D^I_x = D^I_y = D^I_z \) holds [2–11]

\[
D^I_x = D^I_y, \quad D^I_z = D^I_z.
\]

According to our simple diffusion model for fluid molecules in a channel pore, the empirical diffusion tensor \( D^E \) defined by the Einstein relation is not well-defined. The components of \( D^E \) in the directions of confinement involve the observation time: \( D^E_y = D^E_y(t) \) and \( D^E_z = D^E_z(t) \). Different observation times yield different outcomes, see Fig. 2. In contrast, the intrinsic diffusion tensor \( D^I \) defined on the BD theory reproduces the diffusion tensor \( D \) used in the model in all components, see Eq. (4).

This result carries over to more realistic models. In order to account for particle–particle interactions and for interactions with the channel walls, we need to consider diffusion processes subjected to external and internal forces. As far as the BD theory is concerned, these forces are described in terms of drift coefficients. They do, however, not affect the diffusion tensor, which implies...
that the definition of diffusion tensors by means of BD theory is not affected by the presence or absence of external or internal forces. More precisely, the evolution of the MSD components will of course depend for large times on the detailed forces acting on and between the fluid particles in a nanoporous material. However, according to the BD theory, the short time behavior of the MSD is not affected by these forces. Therefore, the intrinsic diffusion coefficient defined by the short time behavior of the MSD, indeed, reflects only the diffusivity properties of the confined fluid.

We have illustrated our main point above using a BD model. However, the proposed approach to transport coefficient is not restricted to BD modeling. All kinds of simulation techniques can be used that allow for the computation of statistical quantities of second order in time such as the MSD. For example, molecular dynamics simulation techniques can be used. Intrinsic transport coefficient can also be computed from experimental data provided that second order statistical quantities can be measured. For example, if single particle tracking by means of tagging can be carried out, single particle trajectories can be recorded from which quantities such as the MSD can be calculated. In this context, pulsed field gradient NMR studies could also be particularly helpful. By means of this technique, the Fourier transformed of the displacement probability density can be measured. The displacement probability density, in turn, provides all information about the second order statistics and allows, for example, to compute the MSD and the intrinsic transport coefficients related to the BD theory.

4. Summary

The objective of this study was the characterization of nanoporous materials in terms of transport coefficients. Primarily, diffusion coefficients have been addressed. We distinguished between empirical and intrinsic diffusion coefficients. The former are related to the Einstein relation and defined by the long time behavior of particles, whereas the latter are related to the theory of Brownian dynamics and defined by the short time behavior of particles. We have demonstrated that empirical coefficients should not be applied because empirical coefficients cannot deal with confinement effects. In contrast, intrinsic coefficients are well-defined and can be applied to all kinds of systems including systems that are confined to bounded domains and consist of interacting particles with relatively large sizes.

References

[1] T.D. Frank, Fluctuation–dissipation theorems for nonlinear Fokker–Planck equations of the Desai–Zwanzig type and Vlasov–Fokker–Planck equations, Phys. Lett. A 329 (2004) 475–485.
[2] T.D. Frank, R. Friedrich, Estimating the nonextensivity of systems from experimental data: a nonlinear diffusion equation approach, Physica A 347 (2005) 65–76.
[3] R. Friedrich, J. Peinke, Description of a turbulent cascade by a Fokker–Planck equation, Phys. Rev. Lett. 78 (1997) 863–866.
[4] J. Gradisek, R. Friedrich, E. Govekar, I. Grabec, Examples of analysis of stochastic processes based on time series data, Meccanica 38 (2003) 33–42.
[5] C. Renner, J. Peinke, R. Friedrich, O. Chanal, B. Chabaud, Universality of small scale turbulence, Phys. Rev. Lett. 89 (2002) 124502.
[6] T.D. Frank, P.J. Beek, R. Friedrich, Fokker–Planck perspective on stochastic delay systems: exact solutions and data analysis of biological systems, Phys. Rev. E 68 (2003) 021912.
[7] R. Friedrich, S. Siegert, J. Peinke, St. Lück, M. Seifert, M. Lindemann, J. Raethjen, G. Deuschl, G. Pfister, Extracting model equations from experimental data, Phys. Lett. A 271 (2000) 217–222.
[8] G.R. Jafari, S.M. Fazeli, F. Ghasemi, S.M.V. Allaei, M.R.R. Tabar, A.I. Zad, G. Kavei, Stochastic analysis and regeneration of rough surfaces, Phys. Rev. Lett. 92 (2004) 226101.
[9] S. Kriso, J. Peinke, R. Friedrich, P. Wagner, Reconstruction of dynamical equations for traffic flow, Phys. Lett. A 299 (2002) 287–291.
[10] H.U. Bödeker, M.C. Röttger, A.W. Liehr, T.D. Frank, R. Friedrich, H.G. Purwins, Noise-covered drift bifurcation of dissipative solitons in a planar gas-discharge system, Phys. Rev. E 67 (2003) 056220.
[11] C.W. Gardiner, Handbook of Stochastic Methods, Springer, Berlin, 1997.