Anomalous Knudsen diffusion and reactions in disordered porous media

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1. Motivation and objectives

In this paper we study the Knudsen diffusion and reactions in the random porous media in terms of continuous time random walk (CTRW) models. The main purpose of the work is to set up a mathematical model describing anomalous transport of molecules, absorption and reaction of molecules on pore walls. Anomalous transport is known to exist in a wide range of physical, chemical and biological situations (see reviews Metzler & Klafter 2000; Metzler & Klafter 2004). The theory of anomalous diffusion is well-established and leads to the integral equations or the alternative fractional diffusion equations for number densities. Despite the progress in understanding the anomalous transport, most work has concentrated on the passive density of the particles, and comparatively little is known about the interaction of non-standard transport with chemical reactions. This paper is intended to address this issue by utilizing the random walk techniques in order to model the Knudsen diffusion with reactions in disordered porous media.

The traditional approach to reaction-transport phenomena is based on reaction-diffusion equations. Its main feature is that the reaction and diffusion processes are separable. It has been discovered recently that this is no longer the case for subdiffusive transport with reactions (Henry *et al.* 2006; Yadav & Horsthemke 2006; Fedotov & Iomin 2007). The memory effects in the random walks result in a non-trivial combination of reactions and spatial transport for densities. Thus new mesoscopic models are necessary to make long-awaited progress in understanding and developing a theoretical description of anomalous transport in the random porous media. Our aims are to (i) use a probabilistic approach for underlying microscopic transport for molecules; (ii) derive mesoscopic balance equations for number densities; (iii) show that the standard mean-field reaction-diffusion equations do not always give the right mesoscopic description; and (iv) validate the models by performing Monte Carlo simulations.

In the Knudsen regime, when the transport is dominated by collisions with the pore walls, the molecules move along the sequence of line segments (chords) connecting the pore surface. The main statistical characteristics of the disordered porous media is the chord length probability density function $f(r)$. Usually it has a power law distribution $f(r) \sim r^{-\mu}$ as $r \to \infty$ and may lead to anomalous transport of molecules (Levitz 1997). It is assumed that a molecule moves a distance r chosen from a probability density function $f(r)$, then it hits the pore wall and changes direction. The new direction is independent of the direction in which it approaches the wall. This can be described by the well-known Knudsen cosine law. Here we approximate the random trajectories of molecules by CTRW, which involves two random time scales τ_f and τ_w. The first one is the flight time, $\tau_f = r/c$, where c is the speed of the molecule, and the second time τ_w is the waiting time of temporal absorption of molecules by the pore surface. One

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can identify two asymptotic regimes: $\tau_f << \tau_w$ and $\tau_f >> \tau_w$ that correspond to the different models: random jumps model and Levy walks (Metzler & Klafter 2000; Metzler & Klafter 2004).

2. Knudsen diffusion, reactions and random walk models

For simplicity we consider the Knudsen diffusion in hypothetical 2-D pore represented by two parallel lines a distance l apart (Malek & Coppens 2005). The interaction of molecules with the pore wall can be described as follows. When a molecule hits the wall, it can either react on the surface with the probability α or it can be temporally absorbed for the time τ_w with the probability $1-\alpha$. It is convenient to consider the horizontal displacement of molecules and corresponding 1-D random walk. The key probabilistic characteristic is the joint probability density function $\Phi(x,t)$ governing the single transition. It gives the probability of making a step of length x within time interval t to $t+dt$. It can be written in the following form

$$\Phi(x,t) = \psi(t|x)\rho(x), \tag{2.1}$$

where $\rho(x)$ is the probability density function to move a distance of length x and $\psi(t|x)$ is the conditional pdf making this displacement in time t. The explicit expression for the function $\rho(x)$ can be found from the standard cosine law: $dp = \frac{1}{2}\cos\theta d\theta$. It gives the probability that the molecule leaves the wall in the direction forming the angle θ with the normal to the surface. From two equations $\rho(x)dx = \frac{1}{2}\cos\theta d\theta$ and $x = l\tan\theta$ (see Fig.1) we obtain

$$\rho(x) = \frac{1}{2l}\left(1+\left(\frac{x}{l}\right)^2\right)^{-\frac{3}{2}}. \tag{2.2}$$

This is an example of a power law distribution for which $\rho(x) \sim x^{-3}$ as $x \to \infty$. In the following we consider the probability density function involving the exponent $\mu > 2$

$$\rho(x) = a\left(1+\left(\frac{x}{l}\right)^2\right)^{-\frac{\mu}{2}} \tag{2.3}$$

with the asymptotic property $\rho(x) \sim x^{-\mu}$ as $x \to \infty$ and the distribution with the cutoff l_{cut}

$$\rho(x) = \begin{cases} a\left(1+\left(\frac{x}{l}\right)^2\right)^{-\frac{\mu}{2}}, & |x| \le l_{cut} \\ 0, & |x| > l_{cut} \end{cases} \tag{2.4}$$

where a is the normalization constant.

When the time of flight τ_f is small compared to the time of absorption τ_w we can use the random jumps model. In this case the function $\Phi(x,t)$ can be written in the decoupled form

$$\Phi(x,t) = \psi(t)\rho(x), \tag{2.5}$$

where $\psi(t)$ is the waiting time distribution for the absorption time τ_w and $\rho(x)$ is the jumps-pdf. This form corresponds to the case when the waiting time and jumps are independent. The survival probability for the molecule to stay at the surface is

$$\Psi(t) = \Pr[t > \tau_w] = \int_t^\infty \psi(\tau)d\tau. \tag{2.6}$$

The anomalous (subdiffusion) regime occurs if the mean waiting time $\overline{\tau} = \int_0^\infty \tau\psi(\tau)d\tau$

is infinite and the variance $\sigma^2 = \int_{R^1} x^2 \rho(x) dx$ is finite. If the asymptotic behavior for the waiting-time density $\psi(t)$ for large t is $t^{-1-\gamma}$ with $0 < \gamma < 1$, the mean waiting time $\overline{\tau} = \infty$ and the mean-squared displacement $\sim \sigma^2 t^\gamma$ (subdiffusion) (Metzler & Klafter 2000). For the finite mean value $\overline{\tau}$, we have the standard diffusion for which the mean-squared displacement is Dt, where

$$D = \frac{\sigma^2}{2\overline{\tau}}. \tag{2.7}$$

Decoupling assumption (2.5) is inappropriate for long jumps x for which our assumption $\tau_f = x/c << \tau_w$ is no longer valid. That is why one needs to consider the jumps-pdf $\rho(x)$ with a finite variance: $\sigma^2 < \infty$ such as Eq. (2.4).

Note that Levy flights correspond to the case when the time of flight τ_r is large compared to the absorption time τ_w. In this case we have a coupled probability density function (2.1) with the pdf $\rho(x)$ for horizontal displacements and the conditional pdf $\psi(t|x)$ to move along the given distance of length x in time t. If all particles move with the constant velocity v, the pdf $\psi(t|x)$ has the form $\psi(t|x) = \delta(x - vt)$. In what follows we consider the random jumps model only.

3. Random jumps models and mesoscopic equations

Now we are in a position to discuss the mesoscopic reaction-transport process in porous media in the Knudsen regime. The main purpose is to show that the standard mean-field reaction-diffusion equations do not always give the right mesoscopic description. We introduce two mesoscopic densities $J(x,t)$ and $n(x,t)$. The first one is the number of molecules reaching the point x at time t. The equation for $J(x,t)$ can be written in terms of joint pdf $\Phi(x,t) = \psi(t)\rho(x)$ and the initial density $n_0(x)$

$$J(x,t) = (1-\alpha)\int_0^t \int_{-\infty}^{\infty} J(x-z, t-\tau)\psi(\tau)\rho(z)dzd\tau + (1-\alpha)\psi(t)\int_{-\infty}^{\infty} n_0(x-z)\,\rho(z)\,dz, \tag{3.1}$$

where α is the probability of annihilation on the surface. The factor $1-\alpha$ takes into account the fact that after collisions with the pore interface, only the fraction of molecules continues the movement. The density of particles $n(x,t)$ at point x at time t can be found in terms of the survival function $\Psi(t)$

$$n(x,t) = (1-\alpha)\int_0^t J(x, t-\tau)\Psi(\tau)\,d\tau + (1-\alpha)n_0(x)\Psi(t). \tag{3.2}$$

The first term on the right-hand side represents the molecules that arrive at position x earlier than t at the time $t-\tau$, and do not jump up to time t and do not annihilate (the factor $1-\alpha$). The second term represents the initial number of molecules that wait at the position x up to time t and do not react.

3.1. *Integro-differential equations*

From the balance equations (3.1) and (3.2) we can find the integro-differential equation for the mesoscopic density $n(x,t)$

$$\frac{\partial n}{\partial t} = \int_0^t K(t-\tau)\int_{-\infty}^{\infty}\left[n(x-z, t-\tau) - n(x,\tau)\right]\rho(z)dzd\tau - \frac{\alpha}{1-\alpha}\int_0^t R(t-\tau)n(\tau)d\tau, \tag{3.3}$$

where the memory kernels $K(t)$ and $R(t)$ have to be determined (see Eq. (4.11)). We derive this equation by using the standard technique of the Laplace transform for $\psi(t)$, the Fourier transform for $\rho(x)$

$$\tilde{\psi}(p) = \int_0^\infty \psi(t) e^{-pt} dt\,, \quad \hat{\rho}(k) = \int_{-\infty}^\infty \rho(x) e^{ikx} dx \tag{3.4}$$

and the Fourier-Laplace (F-L) transform for the densities $J(x,t)$ and $n(x,t)$. From Eqs. (3.1) and (3.2) we obtain

$$\tilde{J}(k,p) = (1-\alpha)\tilde{\psi}(p)\hat{\rho}(k)\left(\tilde{J}(k,p) + \hat{n}_0(k)\right), \tag{3.5}$$

$$\tilde{n}(k,p) = \frac{(1-\alpha)(1-\tilde{\psi}(p))}{p}\left(\tilde{J}(k,p) + \hat{n}_0(k)\right). \tag{3.6}$$

Here we use the standard convolution property

$$\tilde{J}(k,p)\tilde{\psi}(p)\hat{\rho}(k) = \int_0^t \int_{-\infty}^\infty J(x-z, t-\tau)\psi(\tau)\rho(z) e^{-p\tau + ikz}\, dz d\tau$$

and

$$\widetilde{\Psi}(p) = \frac{1-\tilde{\psi}(p)}{p}.$$

Rearranging Eqs. (3.5) and (3.6) and introducing the memory kernels $K(t)$ and $R(t)$ in terms of their Laplace transform:

$$\tilde{K}(p) = \frac{p\tilde{\psi}(p)}{1-\tilde{\psi}(p)}, \qquad \tilde{R}(p) = \frac{p}{1-\tilde{\psi}(p)}, \tag{3.7}$$

we find

$$p\tilde{n}(k,p) - \hat{n}_0(k) = \tilde{K}(p)(\hat{\rho}(k)-1)\tilde{n}(k,p) - \frac{\alpha}{1-\alpha}\tilde{R}(p)\tilde{n}(k,p)\,. \tag{3.8}$$

Applying the inverse F-L transform to Eq. (3.8), we obtain the integro-differential equation (3.3).

One can use the Taylor series in (3.3) expanding $n(x-z, t-\tau)$ in z and truncate the series at the second moment. Equation (3.3) takes the form of local in space differential equation with the memory effects

$$\frac{\partial n}{\partial t} = \frac{\sigma^2}{2}\int_0^t K(t-\tau)\frac{\partial^2 n}{\partial x^2} d\tau - \frac{\alpha}{1-\alpha}\int_0^t R(t-\tau) n(\tau) d\tau, \tag{3.9}$$

where

$$\sigma^2 = \int_{-\infty}^\infty z^2 \rho(z) dz. \tag{3.10}$$

Note that this truncation is valid only when the higher moments become progressively smaller. It is not always the case for the Knudsen diffusion in porous media. For the power law distribution $\rho(x) \sim x^{-\mu}$ as $x \to \infty$, all moments $\mathbf{E}x^m$ diverge for $m \geq \mu - 1$. For this reason, in this section (jumps model) we use only the pdf with the cutoff l_{cut} (2.4) for which all moments are finite. To illustrate the theory let us consider several examples of the waiting time distributions $\psi(t)$.

4. Waiting time distributions

4.1. *Exponential waiting time distribution*

Consider first the classical case when the waiting time pdf is of exponential form

$$\psi(t) = \frac{1}{\tau_w} \exp\left(-\frac{t}{\tau_w}\right). \tag{4.1}$$

The mean waiting time is finite and equals to τ_w. The Laplace transforms are

$$\tilde{\psi}(p) = \frac{1}{1+p\tau_w}, \qquad \tilde{K}(p) = \frac{1}{\tau_w}, \qquad \tilde{R}(p) = \frac{1+p\tau_w}{\tau_w}. \tag{4.2}$$

Since we are interested in the long time limit $t \to \infty$ ($\tau_w << t$), we could consider the asymptotes $p\tau_w \to 0$ and approximate $\tilde{R}(p)$ by the constant τ_w^{-1}. Then the memory kernels in Eq. (3.3) are delta functions:

$$K(t) = R(t) = \frac{1}{\tau_w}\delta(t). \tag{4.3}$$

The equation for the mesoscopic density $n(x,t)$ is

$$\frac{\partial n}{\partial t} = \frac{1}{\tau_w}\int_{-\infty}^{\infty} \left[n(x-z,t) - n(x,t)\right] \rho(z)dz - \frac{\alpha}{\tau_w(1-\alpha)}n. \tag{4.4}$$

This corresponds to the Markovian case for which Eq. (3.3) becomes local in time. If we use the Taylor series expansion for $n(x-z,t)$ in z we obtain the standard reaction-diffusion equation

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \nu n, \tag{4.5}$$

where

$$D = \frac{\sigma^2}{2\tau_w}, \qquad \nu = \frac{\alpha}{\tau_w(1-\alpha)}. \tag{4.6}$$

Equation (4.5) with the initial condition $n(x,0) = n_0(x)$ can then be easily solved.

4.2. *Power law distribution*

Now let us consider the case for which the waiting time density is

$$\psi(t) \sim \left(\frac{\tau_p}{t}\right)^{1+\gamma}, \quad t \to \infty \tag{4.7}$$

where τ_p is the time scale. It follows from Eq. (4.7) that the first moment (the mean waiting time) diverges when $0 < \gamma < 1$. This leads to a slow anomalous diffusion (Metzler & Klafter 2000). For the pdf $\rho(x)$ with a finite variance, $\sigma^2 < \infty$, the mean-squared displacement is

$$\mathbf{E}x^2(t) \sim D_\gamma t^\gamma, \tag{4.8}$$

where D_γ is the generalized diffusion coefficient:

$$D_\gamma = \frac{\sigma^2}{2\tau_p^\gamma}. \tag{4.9}$$

The Laplace transform of $\psi(t)$ for the small p is

$$\tilde{\psi}(p) \approx 1 - C_\gamma\left(p\tau_p\right)^\gamma, \qquad 0 < \gamma < 1 \tag{4.10}$$

(see Metzler & Klafter 2000). The memory kernels $K(t)$ and $R(t)$ in term of their Laplace transforms are

$$\tilde{K}(p) = \tilde{R}(p) \approx \frac{p^{1-\gamma}}{C_\gamma \tau_p^\gamma}. \tag{4.11}$$

From Eq. (3.8), we obtain

$$p\tilde{n}(k,p) - \hat{n}_0(k) = \frac{p^{1-\gamma}}{C_\gamma \tau_p^\gamma}(\hat{\rho}(k) - 1)\tilde{n}(k,p) - \frac{\alpha}{1-\alpha}\frac{p^{1-\gamma}}{C_\gamma \tau_p^\gamma}\tilde{n}(k,p)\,. \tag{4.12}$$

This leads to the temporal fractional differential operator and corresponding anomalous reaction-transport equation for the mesoscopic density $n(x,t)$

$$\frac{\partial n}{\partial t} = \frac{1}{C_\gamma \tau_p^\gamma} D^{1-\gamma} \int_{R^1} \left[n(x-z,t) - n(x,t)\right] \rho(z) dz - \frac{\alpha}{(1-\alpha) C_\gamma \tau_p^\gamma} D^{1-\gamma} n, \tag{4.13}$$

where $D^{1-\gamma}$ is the Riemann-Liouville fractional derivative:

$$D^{1-\gamma} n\,(x,t) = \frac{1}{\Gamma\,(\alpha)} \frac{\partial}{\partial t} \int_0^t \frac{n\,(x,s)\,ds}{(t-s)^{1-\gamma}} \tag{4.14}$$

and $0 < \gamma < 1$. One can see that the memory effects due to the power law for waiting time result in the dependence of the reaction term on transport properties. The reaction and transport processes are not separable and their influence on the rate of change $\frac{\partial n}{\partial t}$ is not a simple sum (Henry *et al.* 2006; Yadav & Horsthemke 2006; Fedotov & Iomin 2007). By using the Taylor series for $n(x-z,t)$ in z we obtain

$$\frac{\partial n}{\partial t} = \frac{\sigma^2}{2 C_\gamma \tau_p^\gamma} D^{1-\gamma} \frac{\partial^2 n}{\partial x^2} - \frac{\alpha}{(1-\alpha) C_\gamma \tau_p^\gamma} D^{1-\gamma} n. \tag{4.15}$$

The analytic solution to this equation can be found in Henry *et al.* (2006).

5. Monte Carlo simulations

The Monte Carlo simulations are performed to validate the proposed model equations. The time evolution of stochastic particles is determined as follows. An initial position of a particle is randomly chosen according to an initial profile of the number density $n_0(x)$. The particle then jumps to a new position with the jump distance δx being randomly chosen from $\rho(\delta x)$. Upon arriving at a new position, it is determined if the particle is absorbed or not, with the probability of the absorption being given by α. For a non-absorbed particle, a waiting time is determined according to a waiting time distribution function. For a random jumps model, where the time of flight is assumed to be much shorter than the waiting time scale, the time elapsed during this one jump is equal to the randomly chosen waiting time. The jump process is repeatedly simulated until the time of the particle reaches a final time of the simulation. Only non-absorbed particles are considered in the evaluation of statistics.

Figure 1 shows the time evolution of the mean squared displacement in Monte Carlo simulations. For the exponential waiting time distribution, both reacting and non-reacting cases follow

$$\mathbf{E}[x_i(t) - x_i(0)]^2 = Dt, \tag{5.1}$$

where $x_i(t)$ is the location of the particle i at time t, $\mathbf{E}$ is the expectation. In Fig. 1(b),

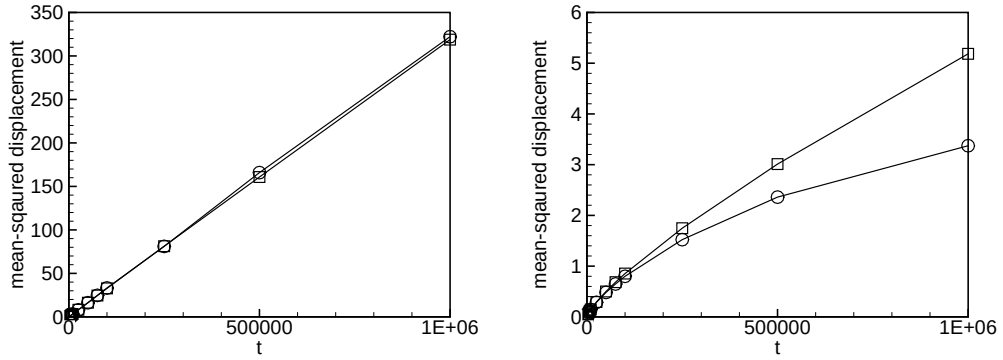

FIGURE 1. Time evolution of the mean-squared displacement in Monte Carlo simulation of the random walk model. The reacting cases (circles) are compared with non-reacting cases (squares). The time is normalized by τ, where τ is τ_w for (a) the exponential waiting time distribution and τ_p for (b) power law waiting time distribution. For the power law waiting time distribution, $\mu = 0.8$. $l_{cut} = 1$. $l = 0.01 l_{cut}$. For the adsorption simulations, $\alpha = 10^{-6}$ for (a) and $\alpha = 10^{-4}$ for (b).

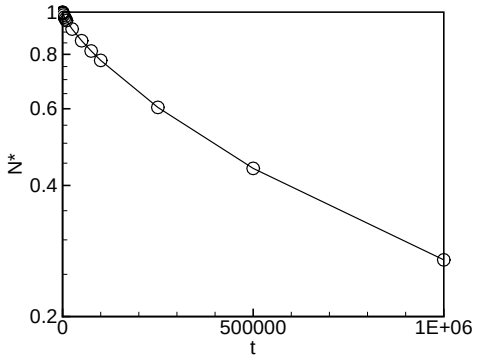

FIGURE 2. Time evolution of the total number of particles, normalized by its initial value, in Monte Carlo simulation of the random walk model with the power law waiting time distribution. The time is normalized by τ_p. $\mu = 0.8$, $l_{cut} = 1$, $l = 0.01 l_{cut}$ and $\alpha = 10^{-4}$.

the results are shown for the power law waiting time distribution given by

$$\psi(t) \sim \left(\frac{\tau_p}{t}\right)^{1.8}. \tag{5.2}$$

The mean-squared displacement for the non-reactive case thus follows

$$\mathbf{E}[x_i(t) - x_i(0)]^2 = D_\gamma t^{0.8}. \tag{5.3}$$

Note that the mean-squared displacement for the reacting case increases more slowly than for the non-reactive case in Fig. 1(b). This shows that the memory effects in the reaction term in Eq. (4.15) also affect the transport process. Overall effects of the reactions are to make particles diffuse more slowly than for the non-reacting case. Figure 2 shows the time evolution of the total number of particles, normalized by its initial value, for the

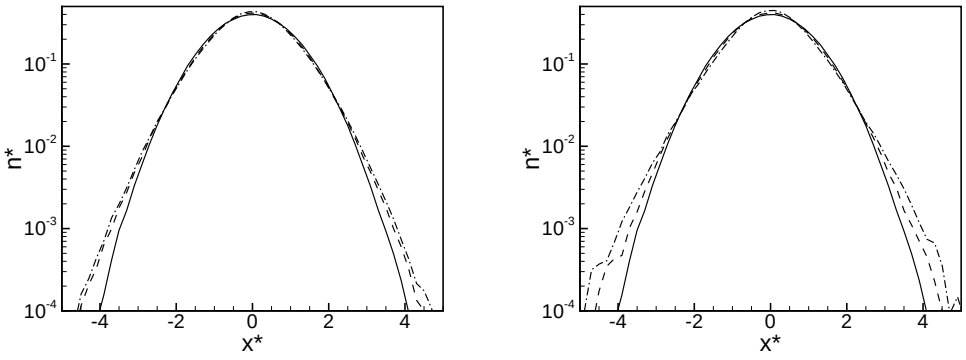

FIGURE 3. Distribution of the normalized number density for (a) the non-reacting case and (b) the reacting case at $t = 0$ (solid lines), $t = 2.5 \times 10^5$ (dashed line) and $t = 1 \times 10^6$ (dashed dotted line). $n^* = n/N$, where N is the total number of particles, and $x^* = x/\sigma$, where σ^2 is the variance of the distribution n. The time is normalized by τ_p. $\mu = 0.8$, $l_{cut} = 1$and $l = 0.01 l_{cut}$. For the reacting case, $\alpha = 10^{-4}$.

power law waiting time distribution (5.2). The memory effects also slow the total reaction rate.

Figure 3 shows the distribution of the normalized number density for the non-reacting and reacting cases at several time instants. The number density initially has the Gaussian distribution. While the number density is not far from the Gaussian, it deviates from the Gaussian at later times, especially at the tails. It is seen that the non-Gaussianity is more pronounced in the reacting case, which is consistent with the time evolution of the mean squared displacement in Fig. 1.

6. Discussion and conclusions

The aim for studying Knudsen diffusion with reactions was to develop insight into the role of anomalous transport and corresponding memory effects for a gas transport in random porous media. The main purpose was to set up mesoscopic equations for the number density by using continuous time random walk (CTRW). The usefulness of CTRW formalism for studying Knudsen diffusion has been noted before by (Levitz 1997; Malek & Coppens 2005), but for the first time we have exploited the anomalous transport in porous media together with chemical reactions. Thus, unlike earlier researchers who dealt with passive diffusion, we have developed the mesoscopic model that describes the anomalous transport together with chemical reactions on the pore walls. We have shown that the standard mean-field reaction-diffusion equations do not always give the right description of the mesoscopic process. It happens when the temporary absorption of particles is modeled with the power law waiting time distribution. In this case temporary trapping of particles not only reduces the Knudsen diffusivity but makes it subdiffusive. Another implication of power law distribution is that the memory effects in the random walks result in the dependence of reaction term on transport characteristics. This dependence slows down the total reaction rate. Monte Carlo results lead us to conclude that anomalous transport gives rise to the essentially non-Gaussian behavior of the number

density. Note that the 1-D model of anomalous diffusion with reactions that we have presented is a simplification of transport and reactions in the real porous random media. But the inclusion of several species and corresponding chemical reactions would make the calculations presented here more applicable to the transport phenomena of gases in disordered media such as solid oxide fuel cells (Larminie & Dicks 2003), etc. Many other extensions of this work are possible. We plan to consider the Levy flights as well as the generalization to the 3-D.

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