

Reconsidering Einstein's Derivation of Diffusion Equation to Provide Solutions Consistent with Nano-Scale and Multi-Scale Physics

Gregory Aranovich

aranovich@jhu.edu

Johns Hopkins University

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Reconsidering Einstein's Derivation of Diffusion Equation to Provide Solutions Consistent with Nano-Scale and Multi-Scale Physics

Gregory Aranovich

Johns Hopkins University
3400 N. Charles Street
Baltimore MD 21218
aranovich@jhu.edu

Abstract

We propose corrections to diffusion equation providing solutions consistent with nano-scale and multi-scale physics. These corrections can be useful for various applications, including nano-technology and turbulent flows.

The problem is that classical diffusion equation (which terms are in the core of fluid dynamics models) does not have information about structure of fluid, and fails, for example, at nano-scale. As we show here, this information was lost due to the way the original equation was derived.

In this paper, we reconsidered Einstein's derivation of diffusion equation to eliminate truncation of higher terms. The results give finite difference equation of mass transport where information about fluid structure is not lost. For this reason, new diffusion equation is consistent with nano-scale and multi-scale physics. This is demonstrated by specific examples.

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Einstein's Evolution Equation for Diffusion in Fluids

Classical Einstein's Approximation Using Truncation

Diffusion equation is a core of modern theory of mass transfer in fluids, and it is used in various versions for numerous applications [1-3]. Classical derivation of diffusion equation goes back to Einstein's theory, where he considered a time step, τ , and probability density, $W(\xi)$, of undergoing a jump ξ . Einstein's equation for temporally-evolved density distribution, $n(x, t)$, can be represented by the following integral equation [4-6]:

$$n(x, t + \tau) = \int_{-\infty}^{\infty} W(\xi) n(x + \xi, t) d\xi \quad (1)$$

where function $W(\xi)$ is symmetric:

$$W(\xi) = W(-\xi) \quad (2)$$

and normalized:

$$\int_{-\infty}^{\infty} W(\xi) d\xi = 1 \quad (3)$$

To derive diffusion equation, Einstein considered expansions

$$n(x, t + \tau) = n(x, t) + \tau \frac{\partial n(x, t)}{\partial t} + \dots \quad (4)$$

$$n(x + \xi, t) = n(x, t) + \xi \frac{\partial n(x, t)}{\partial x} + \frac{\xi^2}{2!} \frac{\partial^2 n(x, t)}{\partial x^2} + \frac{\xi^3}{3!} \frac{\partial^3 n(x, t)}{\partial x^3} + \dots \quad (5)$$

and plugged them into equation (1) to get

$$n(x, t) + \tau \frac{\partial n(x, t)}{\partial t} + \dots = n(x, t) \int_{-\infty}^{\infty} W(\xi) d\xi + \frac{\partial^2 n(x, t)}{\partial x^2} \int_{-\infty}^{\infty} \frac{\xi^2}{2!} W(\xi) d\xi + \frac{\partial^4 n(x, t)}{\partial x^4} \int_{-\infty}^{\infty} \frac{\xi^4}{4!} W(\xi) d\xi + \dots \quad (6)$$

Applying condition (3) to equation (6) gives:

$$\tau \frac{\partial n(x, t)}{\partial t} + \dots = \int_{-\infty}^{\infty} W(\xi) \left[\frac{\xi^2}{2!} \frac{\partial^2 n(x, t)}{\partial x^2} + \frac{\xi^4}{4!} \frac{\partial^4 n(x, t)}{\partial x^4} + \dots \right] d\xi \quad (7)$$

After truncations of "higher" terms, equation (7) can be written as

$$\tau \frac{\partial n(x, t)}{\partial t} = \int_{-\infty}^{\infty} W(\xi) \left[\frac{\xi^2}{2!} \frac{\partial^2 n(x, t)}{\partial x^2} \right] d\xi = \frac{\partial^2 n(x, t)}{\partial x^2} \int_{-\infty}^{\infty} W(\xi) \frac{\xi^2}{2!} d\xi \quad (8)$$

which results in the classical diffusion equation:

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad (9)$$

where

$$D = \frac{1}{\tau} \int_{-\infty}^{\infty} \frac{\xi^2}{2!} W(\xi) d\xi \quad (10)$$

In equation (8), truncation of terms $\frac{\partial^4 n(x, t)}{\partial x^4} \int_{-\infty}^{\infty} \frac{\xi^4}{4!} W(\xi) d\xi$ and higher cannot be generally justified by small values of ξ ; this is because the limits of integration are from $\xi = -\infty$ to $\xi = +\infty$

and derivatives $\frac{\partial^i n(x,t)}{\partial x^i}$ can be large (up to $\pm\infty$). In this paper, we show that such a truncation distorts solutions and “kills” nano-scale and multi-scale physics.

Exact Derivation without Truncation Resulting in Finite Difference Diffusion Model

In equation (5), replacing of ξ by $-\xi$ gives:

$$n(x - \xi, t) = n(x, t) - \xi \frac{\partial n(x,t)}{\partial x} + \frac{\xi^2}{2!} \frac{\partial^2 n(x,t)}{\partial x^2} - \frac{\xi^3}{3!} \frac{\partial^3 n(x,t)}{\partial x^3} + \dots \quad (11)$$

From equations (5) and (11), it follows that

$$n(x + \xi, t) + n(x - \xi, t) = 2n(x, t) + 2\left[\frac{\xi^2}{2!} \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{\xi^4}{4!} \frac{\partial^4 n(x,t)}{\partial x^4} + \dots\right] \quad (12)$$

which results in:

$$\frac{\xi^2}{2!} \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{\xi^4}{4!} \frac{\partial^4 n(x,t)}{\partial x^4} + \dots = \frac{1}{2} [n(x + \xi, t) + n(x - \xi, t)] - n(x, t) \quad (13)$$

Plugging $\tau \frac{\partial n(x,t)}{\partial t} + \dots$ from equation (7) into equation (4) gives:

$$n(x, t + \tau) - n(x, t) = \int_{-\infty}^{\infty} W(\xi) \left[\frac{\xi^2}{2!} \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{\xi^4}{4!} \frac{\partial^4 n(x,t)}{\partial x^4} + \dots \right] d\xi \quad (14)$$

and plugging $\frac{\xi^2}{2!} \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{\xi^4}{4!} \frac{\partial^4 n(x,t)}{\partial x^4} + \dots$ from equation (13) into equation (14) results in the following

$$n(x, t + \tau) - n(x, t) = \frac{1}{2} \int_{-\infty}^{\infty} W(\xi) [n(x + \xi, t) + n(x - \xi, t) - 2n(x, t)] d\xi \quad (15)$$

Note that equation (15) is exact - it follows from Einstein's evolution equation (1) without truncations. This equation indicates that diffusion is governed by the averaging of the finite difference (discrete [23]) Laplacian, $n(x + \xi, t) + n(x - \xi, t) - 2n(x, t)$, not by the second derivative, $\frac{\partial^2 n(x,t)}{\partial x^2}$, as in classical approximation (8).

Solutions for Infinite Space

Solution of equation (15) for infinite space can be analyzed using separation of variables $X(x)$ and $T(t)$, such that:

$$n(x, t) = X(x)T(t) \quad (16)$$

Plugging equation (16) into equation (15) results in:

$$\frac{T(t+\tau)-T(t)}{T(t)} = \frac{1}{2} \int_{-\infty}^{\infty} W(\xi) \frac{X(x+\xi)+X(x-\xi)-2X(x)}{X(x)} d\xi = \text{Const} = -q^2 \quad (17)$$

which gives

$$T(t + \tau) - (1 - q^2)T(t) = 0 \quad (18)$$

$$\text{and} \quad \frac{1}{2} \int_{-\infty}^{\infty} W(\xi) [X(x + \xi) + X(x - \xi)] d\xi - (1 - q^2)X(x) = 0 \quad (19)$$

Partial solution of equation (18) can be considered in the form

$$T_q(t) = A_q \exp(\omega t) \quad (20)$$

which after plugging into equation (18) and after algebraic manipulation gives

$$\omega = \frac{\ln(1-q^2)}{\tau} \quad (21)$$

and

$$T_q(t) = A_q (1 - q^2)^{t/\tau} \quad (22)$$

Partial solution of equation (19) can be considered in the form

$$X_k(x) = B_k \exp(ikx) \quad (23)$$

which after plugging into equation (19) and after algebraic manipulations gives:

$$1 - q^2 = \frac{1}{2} \int_{-\infty}^{\infty} W(\xi) [\exp(ik\xi) + \exp(-ik\xi)] d\xi \quad (24)$$

Then, general solution can be presented in the following form;

$$n(x, t) = \int_{-\infty}^{\infty} C(k) (1 - q^2)^{t/\tau} \exp(ikx) dk \quad (25)$$

At $t = 0$ (initial condition) equation (25) gives

$$n(x, 0) = \int_{-\infty}^{\infty} C(k) \exp(ikx) dk \quad (26)$$

So, equation (25) gives a solution, where coefficients $C(k)$ are defined by expansion of function $n(x, 0)$ in Fourier series, and $q^2(k)$ depends on $W(\xi)$ as defined by equation (24).

Simplifications Illustrating the Role of Truncations

Simplistic Free Path Distributions Satisfying Conditions (2) and (3)

Consider equation (15) with probability density:

$$W(\xi) = \frac{1}{2} \delta(\xi - \lambda) + \frac{1}{2} \delta(\xi + \lambda) \quad (27)$$

where λ is the mean free path, and δ is the Dirac delta function. This form of $W(\xi)$ assumes displacements by steps $\pm \lambda$, which simplifies equation (15), but helps to illustrate the role of truncations in equation (7). In this approximation, time step, τ , is the time between consecutive collisions:

$$\tau = \frac{\lambda}{V} \quad (28)$$

where V is the average velocity of molecules.

Plugging equations (27) and (28) into equation (15) results in:

$$n\left(x, t + \frac{\lambda}{V}\right) - n(x, t) = \frac{1}{2} [n(x + \lambda, t) + n(x - \lambda, t) - 2n(x, t)] \quad (29)$$

For steady state, equation (29) becomes:

$$n(x + \lambda, t) + n(x - \lambda, t) - 2n(x, t) = 0 \quad (30)$$

Obviously, at $\lambda \rightarrow 0$ equation (30) turns into the classical differential equation,

$$\frac{\partial^2 n(x,t)}{\partial x^2} = 0 \quad (31)$$

However, unlike equation (31), equation (30) includes parameter λ , which:

- a) carries information about molecular structure of the fluid, and
- b) determines the scale of diffusion mechanisms.

For this reason, as we show later in this paper, finite difference diffusion equation (30) is consistent with nano-scale and multi-scale physics.

Finite Difference Diffusion Flux and Diffusion Equation

Figure 1 illustrates the model behind equations (27) and (28).

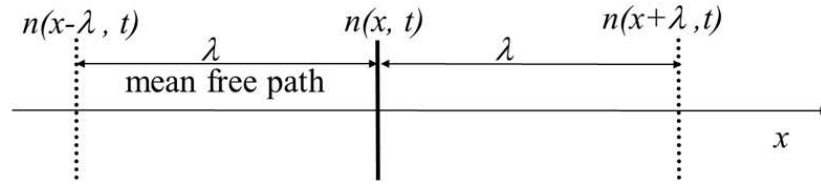


Figure 1. Distribution of molecules between $x - \lambda$ and $x + \lambda$.

Assuming that half of molecules move from left to right and half of them moves from right to left, the resulting flux, $F(x,t)$, can be calculated as:

$$F(x, t) = \frac{1}{2} V [n(x - \lambda, t) - n(x + \lambda, t)] \quad (32)$$

For three-dimensional fluid (diffusing in one direction), factor $\frac{1}{2}$ in equation (32) becomes $\frac{1}{6}$ and this equation becomes:

$$F(x, t) = \frac{1}{6} V [n(x - \lambda, t) - n(x + \lambda, t)] \quad (33)$$

Equations (32) and (33) show that the diffusion flux is determined by the finite difference, $n(x - \lambda, t) - n(x + \lambda, t)$. In particular, for one-dimensional diffusion in three-dimensional space, finite difference functional (33) gives following diffusion equation:

$$\frac{n(x, t + \lambda/V) - n(x, t)}{\lambda/V} = \frac{1}{6} V \frac{[n(x + \lambda) - n(x, t)] - [n(x, t) - n(x - \lambda, t)]}{2\lambda} = D \frac{n(x + \lambda, t) + n(x - \lambda, t) - 2n(x, t)}{4\lambda^2} \quad (34)$$

where

$$D = \frac{1}{3} V \lambda \quad (35)$$

Equation (34) includes V and λ as two independent parameters. At $\lambda \rightarrow 0$, equation (34) turns into classical diffusion equation, where parameters V and λ are combined in one parameter, $D = \frac{1}{3} V \lambda$ [24]. However, in this case, $\frac{1}{3} V \lambda$ can be finite only if V is infinite (which is “unphysical”). So, differential equation is not right math; the right one is finite difference equation where λ is essentially finite.

Usually, in mathematical literature, step size of the discrete Laplacian is a computational parameter, not a physical property. In equation (34), this step size is a physical characteristic, mean free

path, determined by collision area (i.e, by the structure of the fluid and by molecular mechanisms of collisions).

Obviously, equation (35) can be presented in various versions: three-/two-dimensional, with or without drift, with or without boundaries, in combinations with other equations (such as energy and momentum conservation), etc [1-3]. For example, three-dimensional version of equation (35) containing three-dimensional discrete Laplacian can be presented in the following form:

$$\frac{n(x,y,z,t+\lambda/V)-n(x,y,z,t)}{\lambda/V} = D \left[\frac{n(x+\lambda,y,z,t)+n(x-\lambda,y,z,t)-2n(x,y,z,t)}{(2\lambda)^2} + \frac{n(x,y+\lambda,z,t)+n(x,y-\lambda,z,t)-2n(x,y,z,t)}{(2\lambda)^2} + \frac{n(x,y,z+\lambda,t)+n(x,y,z-\lambda,t)-2n(x,y,z,t)}{(2\lambda)^2} \right] \quad (36)$$

Note that generally speaking mean free path can depend on concentration. For example, classical theory of diffusion in gases [24] gives the following correlation between λ and n :

$$\lambda = \frac{1}{\sqrt{2}\sigma n} \quad (37)$$

where n is in units of molecules/m³ and λ is in units of m. Moreover, mean free path can be anisotropic [28] depending on spatial and angular coordinates and time. However, there are cases where value of λ can be constant. For example, this can occur if fluid consists of molecules A and B, where $n_B \gg n_A$; in this case, A molecules collide only with B molecules and λ_A does not depend on n_A and becomes constant if n_B is constant.

Consistency with Nano-Scale Physics: Definition

For the purpose of our consideration here, we define “consistency with nano-scale physics” as possibility to impose boundary conditions related to nano-scale phenomena, such as pair correlation function and density distribution near surfaces (adsorption). Obviously, this definition cannot be general; however, it reflects capability of solutions to capture nano-scale physics.

To illustrate this definition, consider thermodynamic equilibrium limit which can be defined as a steady state with zero flux. For this case, we compare classical and finite difference predictions. For steady state at zero flux, classical model results in:

$$\frac{\partial n}{\partial x} = 0 \quad (38)$$

but finite difference model gives

$$n(x - \lambda) - n(x + \lambda) = 0 \quad (39)$$

Solution of equation (39) is $n(x) = \text{Const}$, which is not consistent with any type of nano-scale behavior. In fact, if $n(x) = \text{const}$, it is impossible to impose conditions of adsorption (with density distribution near surface). It is also impossible to impose density distribution related to pair correlation function [7, 21, 32, 33]. Unlike equation (38), equation (39) has multiple solutions: any periodic function with period 2λ is a solution, and this can be demonstrated by presenting solution of equation (39) in the following form:

$$n(x) = n_0 + \sum_m [A_m \sin\left(m \frac{x}{\lambda} \pi\right) + B_m \cos\left(m \frac{x}{\lambda} \pi\right)] \quad (40)$$

where n_0 is the average concentration, A_m and B_m are arbitrary constants representing amplitudes of possible density fluctuations, and m is the summation index. Note that equation (40) is a Fourier series, where each term satisfies finite difference equation (39). This multiplicity allows numerous types of possible nano-scale behavior. In particular, equation (39) allows local density fluctuations [7, 8] and adsorption variations near surfaces [20], which we consider later in this paper.

Solutions Consistent with Nano-Scale Physics

Consider nano-physics functions characterizing fluid structure and fluid density distribution near surfaces, including pair correlation function [7,21, 32, 33] and density distribution in adsorbed layer [10, 34 - 36]. Here, we show that these functions are solutions to the finite difference diffusion equation. In particular, in the thermodynamic equilibrium limit, these functions can be presented by a Fourier series, where each term satisfies finite difference diffusion equation.

Pair Correlation Function Satisfying Finite Difference Diffusion Equation in Thermodynamic Equilibrium Limit

In equation (40), constants A_m and B_m depend on mechanisms of density fluctuations. Consider local density fluctuations caused by molecule-molecule correlations, which (in statistical mechanics) is described by pair correlation function, $g(x)$ [37]. Note that this function represents local density as a function of distance from a reference particle.

Figure 2 shows an example of pair correlation function, $n(x) = g(x - x_{random})$, for one-dimensional hard core fluid [25] (solid dots). In this Figure, x_{random} is the coordinate of the “central” (random) molecule in units of the diameter of the hard-core molecule and $x > x_{random}$. In Figure 2, solid line shows solution given by equation (40) where coefficients A_m and B_m are defined by equations (41) and (42).

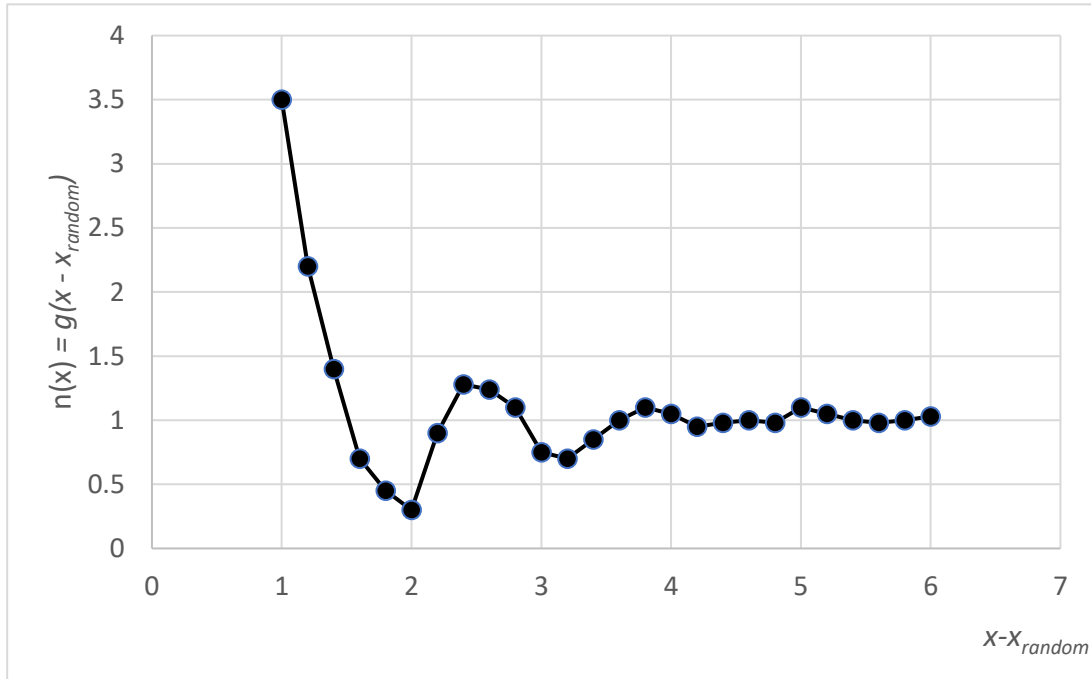


Figure 2. Example of pair correlation function, $n(x) = g(x - x_{random})$, for one-dimensional hard core fluid [25] (solid dots). Here, x_{random} is the coordinate of the “central” (random) molecule in units of the diameter of the hard-core

molecule and $x > x_{random}$. Solid line shows solution given by equation (40) where coefficients A_m and B_m are defined by equations (41) and (42).

Function $n(x)$ in equation (40) becomes equal to the correlation function $g(x - x_{random})$ if constants A_m and B_m are defined as follows:

$$A_m = \int_0^{2\lambda} g(x - x_{random}) \sin\left(m \frac{x}{\lambda} \pi\right) dx \quad (41)$$

and

$$B_m = \int_0^{2\lambda} g(x - x_{random}) \cos\left(m \frac{x}{\lambda} \pi\right) dx \quad (42)$$

This is because conditions (41) and (42) make equation (40) an expansion of $g(x - x_{random})$ in Fourier series. So, pair correlation function $g(x - x_{random})$ satisfies finite difference diffusion equation (39).

Density Distribution Near Surface Satisfying Finite Difference Diffusion Equation

Here, we show that equation (39) is consistent with variation of concentration near surfaces. Consider some adsorption profile, $n_{ads}(x)$, imposed by a surface due to intermolecular and molecule-surface interactions [9, 10]. Solution given by equation (40) becomes consistent with this adsorption profile, if constants A_m and B_m are:

$$A_m = \int_0^{2\lambda} n_{ads}(x) \sin\left(m \frac{x}{\lambda} \pi\right) dx \quad (43)$$

and

$$B_m = \int_0^{2\lambda} n_{ads}(x) \cos\left(m \frac{x}{\lambda} \pi\right) dx \quad (44)$$

and then:

$$n_{ads}(x) = n_0 + \sum_m [A_m \sin\left(m \frac{x}{\lambda} \pi\right) + B_m \cos\left(m \frac{x}{\lambda} \pi\right)] \quad (45)$$

Equation (45) gives the adsorption profile and also satisfies finite difference diffusion equation (39).

Figure 3 shows density distribution for hard disks between hard walls (solid points) obtained by Snook and Henderson from Monte Carlo simulations [21]. Obviously, this density profile is nothing like constant predicted by classical diffusion model (38). Figure 3 also shows predictions of equation (45) (solid line) for $\lambda = 4.5\sigma$ [20] where σ is the diameter of the disk.

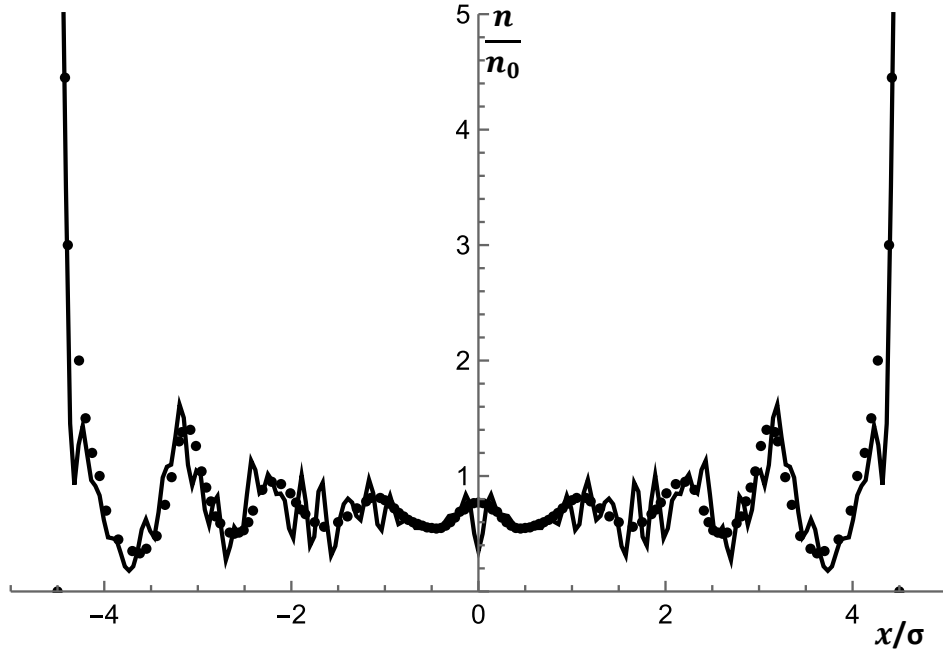


Figure 3. Density distribution for hard disks between hard walls (solid points) obtained by Snook and Henderson from Monte Carlo simulations [21]. Also shown are predictions of equation (45) (solid line) for $\lambda = 4.5\sigma$ [20] where σ is the diameter of the disk.

As seen from Figure 3, finite difference diffusion model is flexible enough to be consistent with adsorption behavior near surfaces

Boundary Conditions for Finite Difference Diffusion Equation Representing Adsorption Mechanisms

Consider adsorption mechanisms determining function $n_{ads}(x, t)$ characterizing density distribution near surface. Figure 4 shows a monolayer adsorption with $n(0, t) = n_{ads}(0, t)$; however, our analysis can be generalized for other types of adsorption behavior [29], not only monolayer.

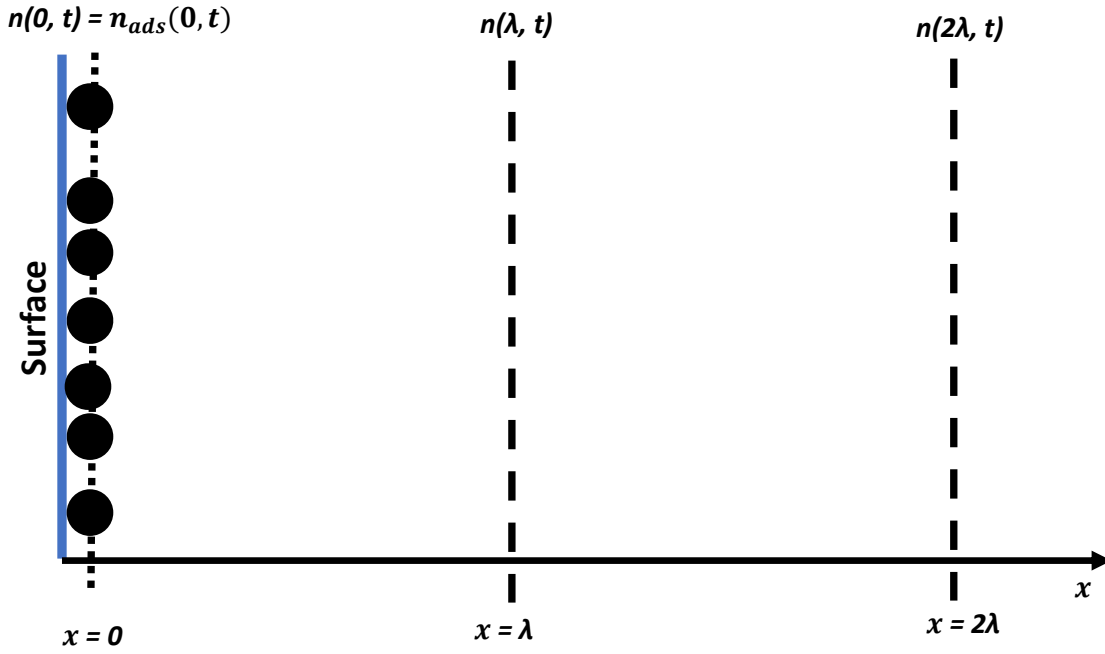


Figure 4. Distribution of the fluid density near a surface.

The flux at $x = \lambda$ can be presented as follows [30, 31]:

$$F(\lambda, t) = a(t)f \exp \frac{\varepsilon_0 + \frac{z\varepsilon a(t)}{a_0}}{kT} - \frac{1}{6} V n(2\lambda, t) \quad (46)$$

In equation (46), the term $a(t)f \exp \frac{\varepsilon_0 + z\varepsilon a(t)/a_0}{kT}$ represents flux from the surface to the bulk, where

- $a(t)$ is the number of adsorbed molecules per surface area;
- f is the frequency of molecular vibrations (which typically is $10^{-13} \dots 10^{-14}$ Hz [30]);
- z is the coordination number in adsorbed layer (usually $z = 6$ for hexagonal symmetry);
- ε_0 and ε are energies of molecule-surface and molecule-molecule interactions (including components of van der Waals interactions and energies of hydrogen/chemical bonding);
- a_0 is the adsorption capacity;
- k is the Boltzmann constant.

Note that the term $\varepsilon_0 + z\varepsilon a(t)/a_0$ is the energy of adsorbed molecules in the mean field approximation [9, 10]. In equation (46), the term $\frac{1}{6} V n(2\lambda, t)$ represents flux from $x = \lambda$ to $x = 0$; this term is analogous to the terms in equation (33) (for three-dimensional case).

At thermodynamic equilibrium where $F(\lambda, t) = 0$, $a(t) = \text{Const} = a$, and $n(2\lambda, t) = n(2\lambda)$, equation (46) can be written as:

$$a f \exp \frac{\varepsilon_0 + \frac{z\varepsilon a}{a_0}}{kT} - \frac{1}{6} V n(2\lambda) = 0 \quad (47)$$

which gives:

$$n(2\lambda) = \frac{6af}{V} \exp \frac{\varepsilon_0 + \frac{z\varepsilon a}{a_0}}{kT} \quad (48)$$

Equation (48) is the boundary condition reflecting adsorption mechanisms influencing density distribution near a surface. This boundary condition can be generalized to reflect various mechanisms of intermolecular interactions in fluids near surfaces.

Multi-Scale Mean Free Path

Multi-Scale at Variable λ

Consider one-dimensional diffusion (as shown in Figure 5), where density is higher at one end and lower at another end. It could be a gas diffusing through a pipe with atmospheric pressure at one end and vacuum at another end (common real situation, such as in pumps or in rocket nozzles). Figure 5 illustrates fluid density distribution, $n(x)$, in the pipe from $n_0 = n(0)$ at $x = 0$ to $n_L = n(L)$ at $x = L$.

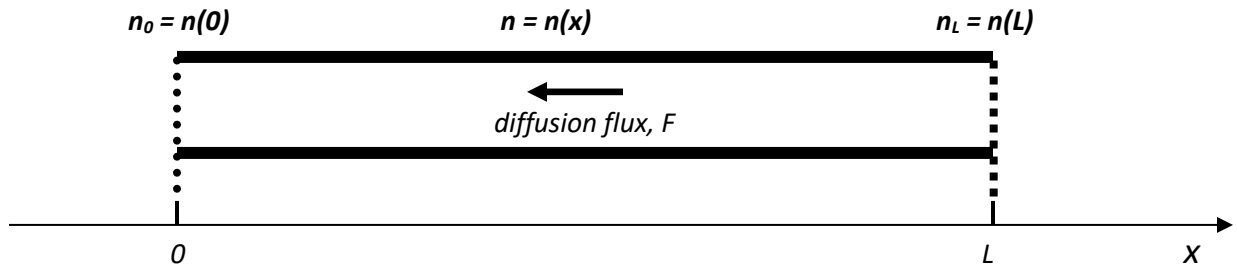


Figure 5. Fluid density, $n(x)$, in the pipe changes from $n_0 = n(0)$ at $x = 0$ to $n_L = n(L)$ at $x = L$.

In the example in Figure 6, value of λ is variable, and the range of these variations could be essentially unlimited (theoretically, from zero to infinity).

Classical Approximation Predicts Unphysical Flux

For the system in Figure 5, consider a steady state with $\frac{\partial n}{\partial t} = 0$ at all x . Then, classical approximation gives:

$$D_{\text{one-dimensional}} \frac{\partial n(x)}{\partial x} = \frac{1}{2} V \lambda(x) \frac{\partial n(x)}{\partial x} = \text{Const} = F \quad (49)$$

i.e.:

$$F = \frac{1}{2} V \lambda(x) \frac{\partial n(x)}{\partial x} \quad (50)$$

Here, F is the flux through the system and $\lambda(x)$ is [24]

$$\lambda(x) = \frac{1}{\sqrt{2} \sigma n(x)} \quad (51)$$

Plugging equation (51) into equation (50) results in:

$$F = \frac{V}{2\sqrt{2} \sigma n(x)} \frac{\partial n(x)}{\partial x} \quad (52)$$

After integration in equation (52), we have:

$$\ln n(x) = \frac{2\sqrt{2}\sigma}{V}Fx + B \quad (53)$$

where B is a constant of integration.

After Imposing boundary conditions, $n(0) = n_0$ and $n(L) = n_L$, and after algebraic manipulations, equation (53) becomes:

$$\frac{n(x)}{n_0} = \left(\frac{n_L}{n_0}\right)^{x/L} \quad (54)$$

Equation (54) gives:

$$\frac{\partial n(x)}{\partial x} = \frac{n_0}{L} \left(\ln \frac{n_L}{n_0}\right) \left(\frac{n_L}{n_0}\right)^{x/L} \quad (55)$$

Plugging $\frac{\partial n(x)}{\partial x}$ and $n(x)$ from equations (54) and (55) into equation (52) results in the following equation for the flux from the classical approximation:

$$F = \frac{V}{\sqrt{2}\sigma L} \ln \frac{n_L}{n_0} \quad (56)$$

As seen from equation (56), classical flux manifests unphysical behavior at $\frac{n_0}{n_L} \rightarrow 0$, because F diverges at $\frac{n_0}{n_L} \rightarrow 0$.

Flux Predicted by Finite Difference Diffusion Equation

For the system illustrated in Figure 5, finite difference equation for steady state flux, F , can be written as follows:

$$F = \frac{1}{2}V\{n[x - \lambda(x)] - n[x + \lambda(x)]\} \quad (57)$$

$$\text{or} \quad n[x - \lambda(x)] - n[x + \lambda(x)] = \frac{2F}{V} \quad (58)$$

Consider solution of finite difference equation (58) in the following form:

$$n(x) = a_x x + b \quad (59)$$

where a_x is a function of x , and b is a constant. Plugging $n(x)$ from equation (59) into equation (58) gives:

$$a_{x+\lambda}[x + \lambda(x)] + b - a_{x-\lambda}[(x - \lambda(x))] - b = \frac{2F}{V} \quad (60)$$

To find the first approximation, consider a_x as a slow function of x , so that

$$a_{x+\lambda} \approx a_{x-\lambda} \approx a_x \quad (61)$$

Then, equation (60) gives

$$a_x \approx \frac{F}{V\lambda(x)} \quad (62)$$

Combining equations (61) and (62) results in

$$a_x \approx \frac{\sqrt{2}\sigma F}{V} n(x) \quad (63)$$

Note that approximation (61) is mathematically compatible with equation (63) if $n(x)$ does not significantly change between $x + \lambda$ and $x - \lambda$. At the high density end, this is possible due to small λ ; and,

at the low density end, this is possible if the density gradient is small. For more accurate calculation, mean free path can be considered anisotropic [28], but this goes beyond our consideration in this paper.

Equations (59) and (63) result in:

$$n(x) = \frac{\sqrt{2}\sigma F}{V} x n(x) + b \quad (64)$$

Solving equation (64) with respect to $n(x)$ gives

$$n(x) = \frac{bV}{V - \sqrt{2}\sigma Fx} \quad (65)$$

From boundary conditions, $n(0) = n_0$ and $n(L) = n_L$, we have from equations (64) and (65):

$$b = n_0 \quad (66)$$

and

$$n(L) = n_L = \frac{n_0 V}{V - \sqrt{2}\sigma FL} \quad (67)$$

Using equations (66) and (67) to eliminate b and F in equation (64) gives:

$$\frac{n(x)}{n_0} = \frac{n_L}{n_L - (n_L - n_0)x/L} \quad (68)$$

Solving equation (67) with respect to F results in:

$$F = \frac{V}{\sqrt{2}\sigma L} \left(1 - \frac{n_0}{n_L}\right) \quad (69)$$

Equation (69) gives the flux in the system on Figure 5 derived from the finite difference equation (58). Unlike classical approximation (54), equation (69) does not manifest unphysical behavior (singularity) at $\frac{n_0}{n_L} \rightarrow 0$. This improvement is the result of using finite difference diffusion model without (classical) truncation. Moreover, at $n_0 \rightarrow 0$, equation (56) gives the following limit of flux:

$$F = \frac{V}{\sqrt{2}\sigma L} = \frac{V n_0}{\sqrt{2}\sigma n_0 L} = V n_0 \frac{\lambda_0}{L} \quad (70)$$

where $\lambda_0 = \frac{1}{\sqrt{2}\sigma n_0}$. This limit is reasonable because, at vacuum conditions, value of $V n_0$ represents “one way” flux where molecules move without collisions.

Comparisons between Classical Approximation and Finite Difference Model

Figure 6 shows dependence of n/n_0 on x/L predicted by classical approximation (equation (54), thin lines) and by finite difference model (equation (68), thick lines) for various for n_0/n_L . As seen from Figure 6, finite difference equation predicts significant deviations from the classical model.

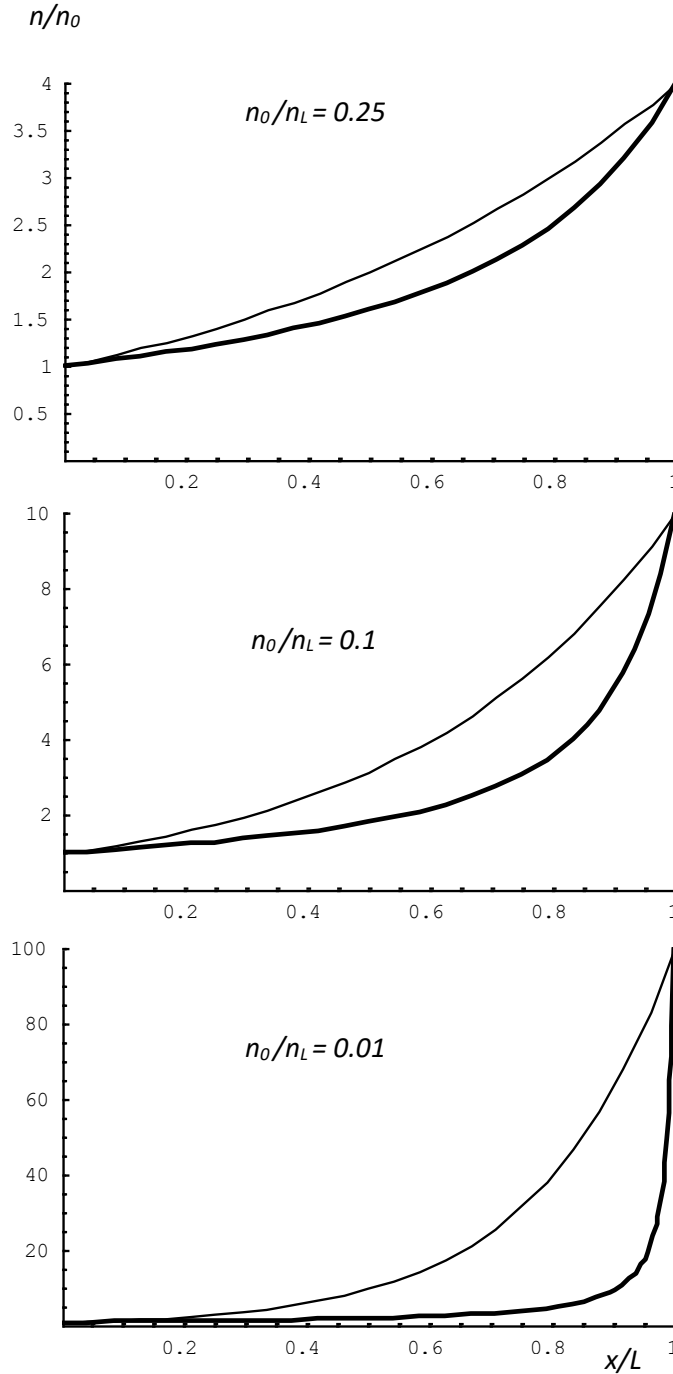


Figure 6. Dependence of n/n_0 on x/L predicted by equations (54) (thin lines) and (68) (thick lines) for various for n_0/n_L . Finite difference equation predicts significant deviations from classical model.

Figure 7 shows steady state flux through the system in Figure 6 as a function of n_0/n_L predicted by classical approximation (56) (thin line) and by equation (69) derived from finite difference model (thick line). As seen from equation (56) and from Figure 8, classical approximation predicts unphysical behavior (singularity) at $\frac{n_0}{n_L} \rightarrow 0$. Finite difference model corrects this defect, and this improvement is due to using diffusion model without truncations.

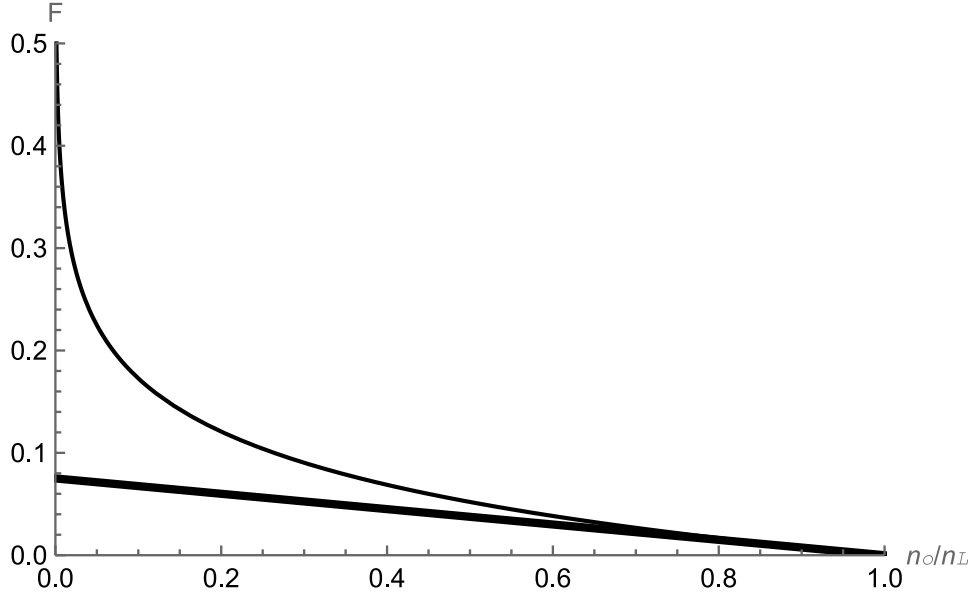


Figure 7. Flux in units of $\frac{v}{\sigma_L}$ as a function of n_0/n_L predicted by classical approximation (56) (thin line) and by finite difference equation (69) (thick line). As seen from equation (56) and from this Figure, classical approximation predicts unphysical behavior (singularity) at $\frac{n_0}{n_L} \rightarrow 0$. Finite difference model corrects this defect, and this improvement is due to using diffusion model without truncations.

Correlations between Points of Consecutive Collisions

One of the key features of classical diffusion model is that the diffusion process is Markovian [13, 18], i.e. collisions of molecules occur at random points at random times. Mathematical aspects of this assumption were widely discussed, and possible deviations from Markovian behavior were analyzed in mathematical literature [11-19]. However, physical aspects of diffusion mechanisms in fluids were never discussed in detail in terms of Markovian/Non-Markovian behavior. Though, there was a recognition that there are fundamental reasons for deviation of diffusion in real fluids from Markovian behavior; in particular, van Kampen wrote that “individual jumps ... cannot be infinitely small” [13, page 3] and therefore real diffusion process does not satisfy mathematical requirements for Markovian process.

For fluids, the scale of diffusion mechanisms is determined by the mean free path, λ . Consider a theoretical example, an ideal gas, where by definition molecules are points of no size, and each molecule moves independently with a constant speed without collisions. Then, theoretically speaking, $\lambda = \infty$, and there are no random events. Obviously, diffusion of such ideal gas is Non-Markovian.

In real fluids, molecules have a finite cross-section/collision area, σ , and finite mean free path, λ . Consider two consecutive collisions where locations of these collisions are illustrated in Figure 8: black thick dot in the center is the point of the “first” collision; locations in the area called “red” are very close to the point of the “first” collision, where the “second” collision is not very likely (especially for rare fluid); locations in the area called “pink” are too distant, where probability of the “second” collision dramatically decays; and there is a “green” area where the “second” collision is most likely. So, there is a correlation between two consecutive collisions: the “second” collision point is not absolutely random because it will (most likely) occur in a “green” area of Figure 8.

Diffusion in fluid includes both stochastic and non-stochastic components; stochastic is collisions at “random” points and “random” angles, and non-stochastic is motion between consecutive collisions. Since frequency of molecular vibrations, f , is $10^{13} \dots 10^{14}$ Hz, collision time is about $1/f$ which gives $10^{-13} \dots 10^{-14}$ sec. Duration of motion between collisions can be estimated as λ / V ; for instance, for air at normal conditions, $\lambda \approx 5 \times 10^{-8}$ m and $V \approx 500$ m/sec, which gives $\lambda / V \approx 10^{-10}$ sec. So, for this example, non-stochastic event lasts 1000...10000 times longer than stochastic one. If λ / V goes down, “fraction” of stochastic component goes up; and if λ / V goes up, “fraction” of non-stochastic component goes up.

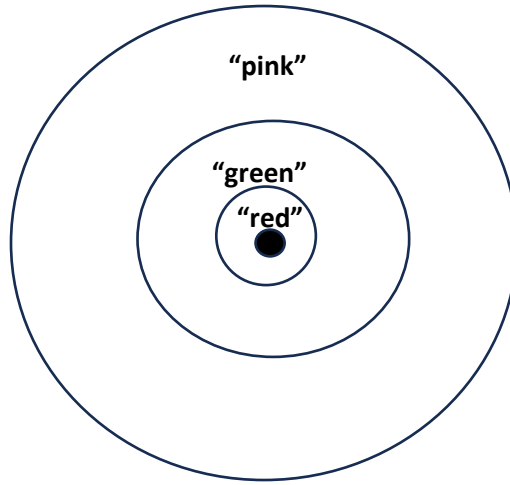


Figure 8. Locations of two consecutive collisions in fluid. Thick black point in the center is the point of the “first” collision. Locations in the area called “red” are very close to the point of the “first” collision, where the “second” collision is not very likely (especially for rare fluid); locations in the area called “pink” are too distant, where probability of the “second” collision dramatically decays; and there is a “green” area where the “second” collision is most likely. So, there is a correlation between two consecutive collisions: the “second” collision point is not absolutely random because it will (most likely) occur in a “green” area.

Table 1 lists various types of diffusion behavior with different scales of λ : ideal gas, gas at Knudsen conditions [22], homogeneous fluids with finite λ , inhomogeneous fluids with variable λ , and classical diffusion model with $\lambda \rightarrow 0$. As seen from Table 1, In terms of mean free path, real fluids (including Knudsen’s gas) are intermediate between absolutely deterministic (“ballistic”) ideal gas (with $\lambda = \infty$) and theoretically Markovian (with $\lambda \rightarrow 0$).

Table 1.

Fluid/Model	Ideal Gas	Knudsen Gas	Homogeneous Fluids	Inhomogeneous Fluids	Classical Diffusion Model
Scale (determined by λ)	$\lambda = \infty$	large λ	finite λ	variable λ , between 0 and ∞	$\lambda \rightarrow 0$
Markovian/Non-Markovian (Deterministic)	Absolutely Deterministic	Deterministic	Mixed	Mixed	Theoretically Markovian
Comments	No collisions	Rare collisions	Correlations between 2 consecutive collisions	Variable Finite Differences	At $\lambda \rightarrow 0$, D can be finite only if V is infinite ($D = \frac{1}{3} V \lambda$)

As shown in Table 1, real fluids include both Markovian and deterministic events.

Conclusions

Classical approximation of diffusion behavior eliminates mean free path, λ , as an independent parameter. However, λ determines the scale of diffusion mechanisms, and it is the only parameter carrying information about structure of the fluid.

Here, we used Einstein's integral evolution equation to derive diffusion equation without truncation (i.e., without elimination of λ as an independent parameter). With this correction, diffusion model turns into finite difference equation. This eliminates fundamental defects of the classical diffusion equation (such as causality problem and "killing" nano- and multi-scale physics).

In this paper, we analyzed consistency of diffusion model with nano-scale physics functions (such as pair correlation function and density distribution near surface) reflecting nano-structure of fluids and adsorption behavior. In particular, we have shown that pair correlation function and density distribution near surface can be expanded in Fourier series where each term satisfies finite difference diffusion equation. We also analyzed possible boundary conditions for finite difference diffusion equation, which represent adsorption mechanisms near surfaces. Our analysis indicates that finite difference diffusion model is consistent with nano-scale physics of fluid structure and with fluid behavior near surfaces.

In this paper, we also considered consistency of finite difference diffusion model with multi-scale behavior where mean free path varies between very low and very high levels. We have shown that finite difference diffusion equation predicts correct behavior of diffusion flux in multi-scale examples where classical approximation predicts unphysical behavior (such as flux singularity).

Based on these results, we can conclude that:

- reducing diffusion model to differential equation "kills" nano-scale and multi-scale physics;
- correlations between consecutive collisions in fluid carry memory effects; this makes fluid diffusion Non-Markovian, and diffusion model cannot be reduced to differential equation;
- finite difference diffusion equation is consistent with exact Einstein's evolution equation;

- the step size of the finite difference diffusion equation is determined by the mean free path carrying information about fluid structure (in particular, about intermolecular interactions and collision mechanisms).

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