Diffusion in Confined Geometries

Quasi 1-dimensional effective diffusion equation

Hokkaido Institute of Technology
Naohisa Ogawa

Talk at Tokyo University
on 4th October 2012

拡散方程式の変化

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

外力

幾何学的拘束条件

有効拡散方程式

- 拡散係数の変化
- 異方性（テンソル）
- 異常拡散流

1．外力による拡散係数の変化

磁場中の荷電粒子の拡散

電荷密度 $n(x,t)$ 電流密度 $\vec{J}(x,t)$ 移動度 μ

$$\begin{cases} \vec{J} = \underbrace{-D\vec{\nabla} n}_{\text{拡散流}} + \underbrace{\mu n \vec{F}_{ext}}_{\text{ドリフト流}} \\ \vec{F}_{ext} = q\vec{v} \times \vec{B} = q\,\vec{J} \times \vec{B}\,/\,n \end{cases}$$

Z軸方向の磁場に対して

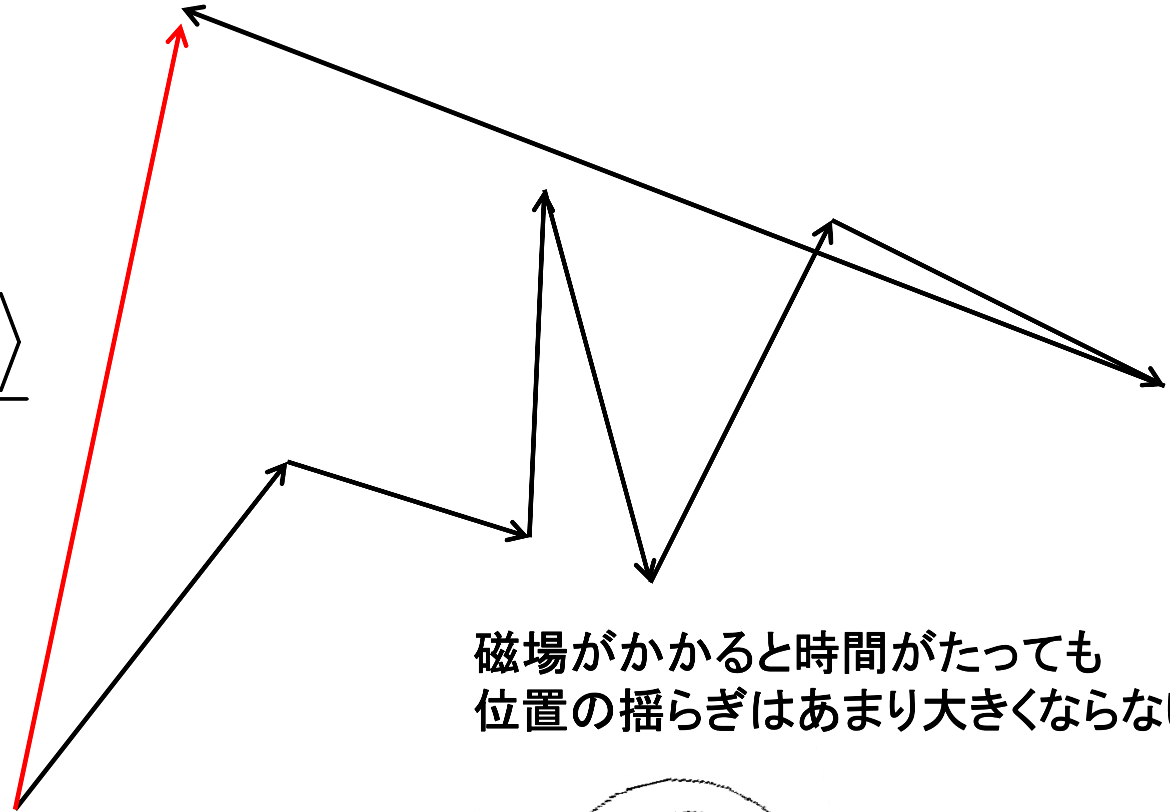
$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = -D\vec{\nabla} n + \underline{\mu q B}_{\varepsilon} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix}$$

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = -D \begin{pmatrix} 1 & -\varepsilon & 0 \\ \varepsilon & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}^{-1} \begin{pmatrix} \vec{\nabla} n \end{pmatrix} = -D \begin{pmatrix} \dfrac{\partial_x n}{1+(\mu q B)^2} \\ \dfrac{\partial_y n}{1+(\mu q B)^2} \\ \partial_z n \end{pmatrix}$$

$$D \to D_{eff} = \frac{D}{1+(\mu q B)^2} \quad for \quad x, y$$

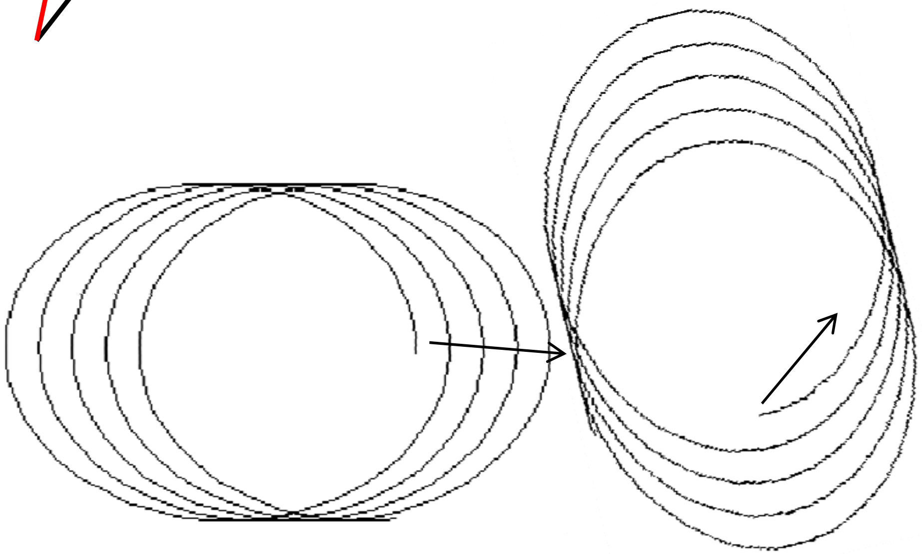
磁場なし

$$D = \frac{\left\langle (\Delta x)^2 \right\rangle}{\Delta t}$$



磁場がかかると時間がたっても
位置の揺らぎはあまり大きくならない

磁場あり



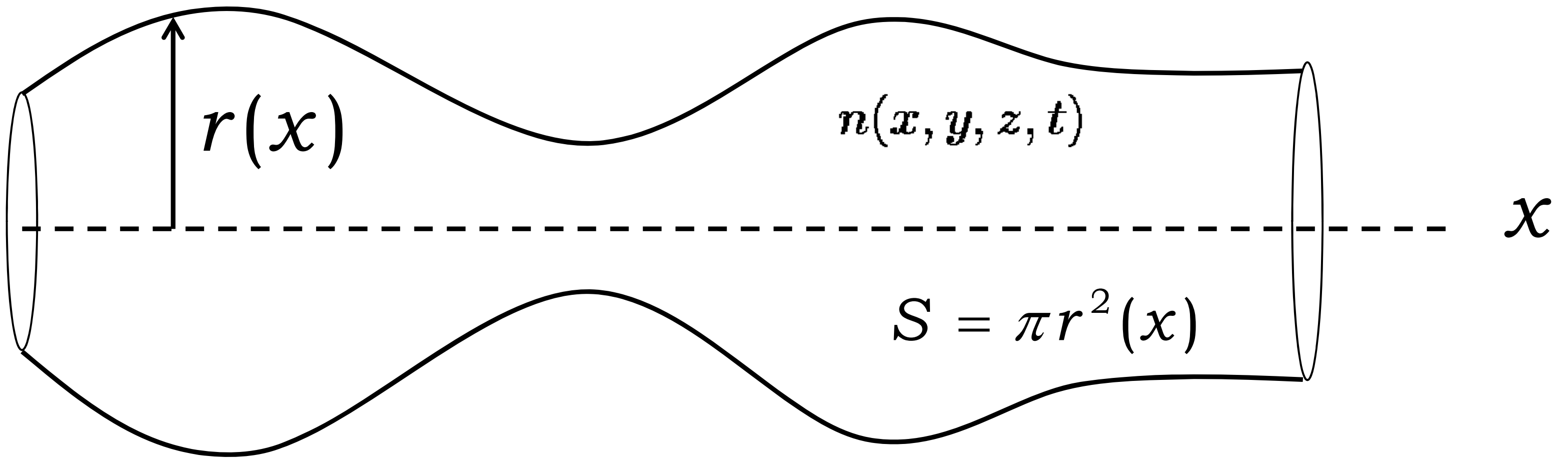
２．幾何学的拘束による
拡散方程式の変化

太さの変化するチューブ内の拡散

○　細胞膜やゼオライトでの拡散現象

○　多孔質媒体での触媒反応

3次元→1次元



$$J_x(x,y,z) = -D\frac{\partial n}{\partial x}, \qquad N(x,t) = \int n \; dydz$$

$$Q_x(x) = \int J_x dydz \approx -DS(x)\frac{\partial}{\partial x}(N/S)$$

$$-\frac{\partial N}{\partial t} = \frac{\partial Q_x}{\partial x} = -D\frac{\partial}{\partial x}S\frac{\partial}{\partial x}\left(\frac{N}{S}\right)$$

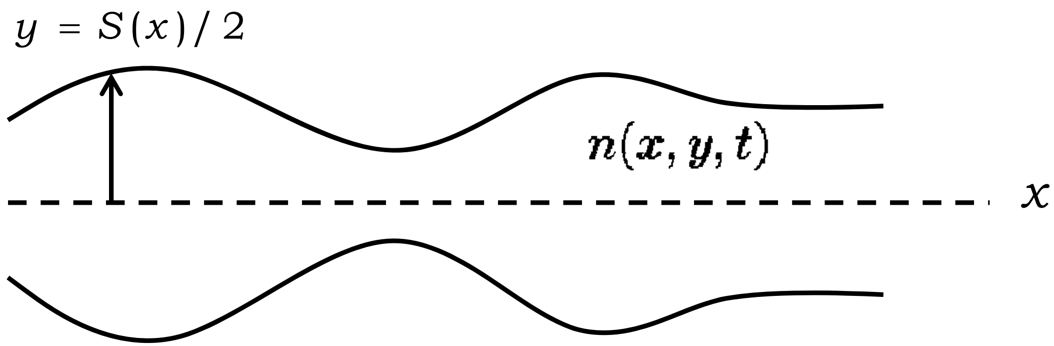
Ficks-Jacob Equation

$$\frac{\partial N}{\partial t} = D\frac{\partial}{\partial x}S\frac{\partial}{\partial x}\frac{N}{S}$$

$d=3 \rightarrow d=1:$ $S(x)=$ 断面積 $N=\int_{y^2+z^2<r^2} dydz\ n(x,y,z,t)$

$d=2 \rightarrow d=1:$ $S(x)=$ 間隔 $N=\int_{-S/2}^{S/2} dy\ n(x,y,t)$

$d=2$



これ以降、簡単のためd=2で議論する

Ficks-Jacob近似の問題点

- $n \longrightarrow N/S$ の近似: 断面内の分布は一定(局所平衡の仮定)
- チューブの境界での境界条件のあいまいさ

よりよい近似の1次元方程式をどうやって作るか?

FJ eq. is Analogeous to Smoluchowski eq.

$$-\frac{\partial N}{\partial t} = -D\frac{\partial}{\partial x}S\frac{\partial}{\partial x}\frac{N}{S}$$
$$= \frac{\partial}{\partial x}\{-D\frac{\partial N}{\partial x} + D(\frac{\partial_x S}{S})N\}$$

$$S \to e^{-U/kT}$$

μ :移動度

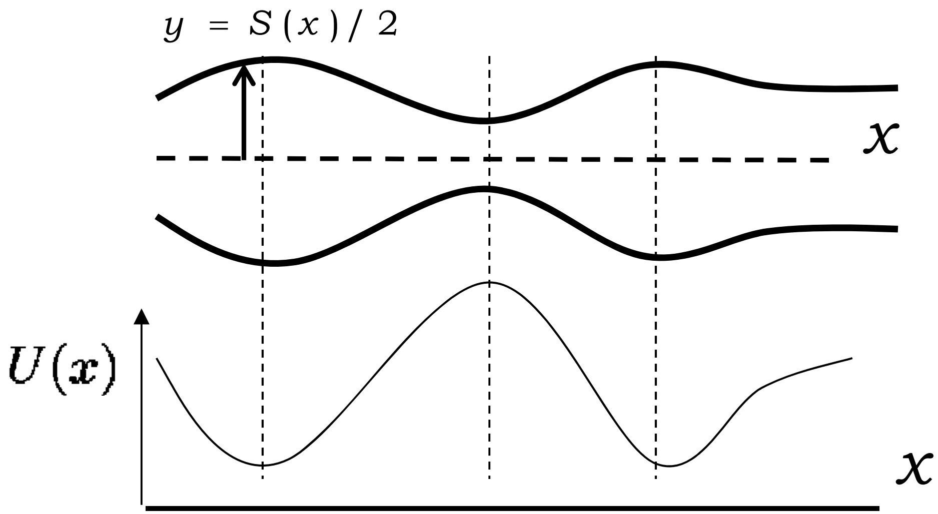
$$-\frac{\partial N}{\partial t} = \frac{\partial J_x}{\partial x}, \quad J_x = -D\frac{\partial N}{\partial x} - \frac{D}{kT}\frac{\partial U}{\partial x}N.$$

FJ eq. = Smoluchowski eq.

FJ eq. :幾何学的拘束下での擬似1次元拡散方程式

$$S \to e^{-U/kT}$$

Smoluchowski eq. :ポテンシャルのある1次元拡散方程式



断面積が小さい、くびれた部分は、高いポテンシャルエネルギーに対応

2次元　Smoluchowski eq.　からの出発

$$\frac{\partial n(x,y,t)}{\partial t} = D\frac{\partial}{\partial x}e^{-\beta U(x,y)}\frac{\partial}{\partial x}e^{+\beta U(x,y)}n + D\frac{\partial}{\partial y}e^{-\beta U(x,y)}\frac{\partial}{\partial y}e^{+\beta U(x,y)}n$$

U はSquare Well ポテンシャルで、

$$U(x,|y| \geq S/2) = \infty, \quad U(x,|y| < S/2) = 0$$

1. チューブ内　$-S/2 < y < S/2$　**では通常の拡散方程式**

2. PotentialのConfining効果で、チューブの外に粒子は出ない

1次元へのReduction

2次元 Smoluchowski eq. の y方向積分

$$\frac{\partial N(x,t)}{\partial t} = D\frac{\partial}{\partial x}\int_{-\infty}^{\infty} dy\ e^{-\beta U(x,y)}\frac{\partial}{\partial x}e^{+\beta U(x,y)}n.$$

$$N(x,t) \equiv \int_{-\infty}^{\infty} n(x,y,t)dy$$

$$\rho(x,y) \equiv \frac{e^{-\beta U(x,y)}}{\int dy\ e^{-\beta U(x,y)}} \quad \left(\int dy\ \rho(x,y) = 1\right)$$

局所平衡の近似:　$n(x,y,t) \sim \rho(x,y)N(x,t)$

$$\frac{\partial N(x,t)}{\partial t} = D\frac{\partial}{\partial x}\, e^{-\beta F}\frac{\partial}{\partial x}e^{+\beta F}N.$$

1次元 Smoluchowski方程式　＝ FJ 方程式

ここで、 $$e^{-\beta F(x)} \equiv \int dy\; e^{-\beta U(x,y)} = S(x)$$

近似の意味: $$J_y = [-D\frac{\partial}{\partial y} - \mu\frac{\partial U}{\partial y}]\rho N = 0.$$

近似の改良

$$n(x,y,t) = \rho(x,y)N(x,t) + \delta n(x,y,t)$$

↓ 代入

$$\begin{cases} \dfrac{\partial N(x,t)}{\partial t} = D\dfrac{\partial}{\partial x}\displaystyle\int_{-\infty}^{\infty} dy\ e^{-\beta U(x,y)}\dfrac{\partial}{\partial x}e^{+\beta U(x,y)}n. \quad \cdots\cdot (A) \\ \dfrac{\partial n(x,y,t)}{\partial t} = D\dfrac{\partial}{\partial x}e^{-\beta U(x,y)}\dfrac{\partial}{\partial x}e^{+\beta U(x,y)}n + D\dfrac{\partial}{\partial y}e^{-\beta U(x,y)}\dfrac{\partial}{\partial y}e^{+\beta U(x,y)}n \end{cases}$$

$\delta n(x,y,t)$ を求めて、(A) に代入。

$$\frac{\partial N(x,t)}{\partial t} = \frac{\partial}{\partial x}\ D(x)\ e^{-\beta F}\frac{\partial}{\partial x}e^{+\beta F}N.$$

有効拡散係数

$$D(x) = \frac{1}{\{1 + r'(x)^2\}^{\lambda}}$$

$$\lambda = \begin{cases} 1/3 & (d=2) \\ 1/2 & (d=3) \end{cases}$$

Zwanzig ’92 J.Phys.Chem., Reguera, Rubi ’01 Phys.Rev.E,

Kalinay, Percus ’06, Phys.Rev. E

3.　曲がったチューブ内での拡散

Diffusion in Curved Tube

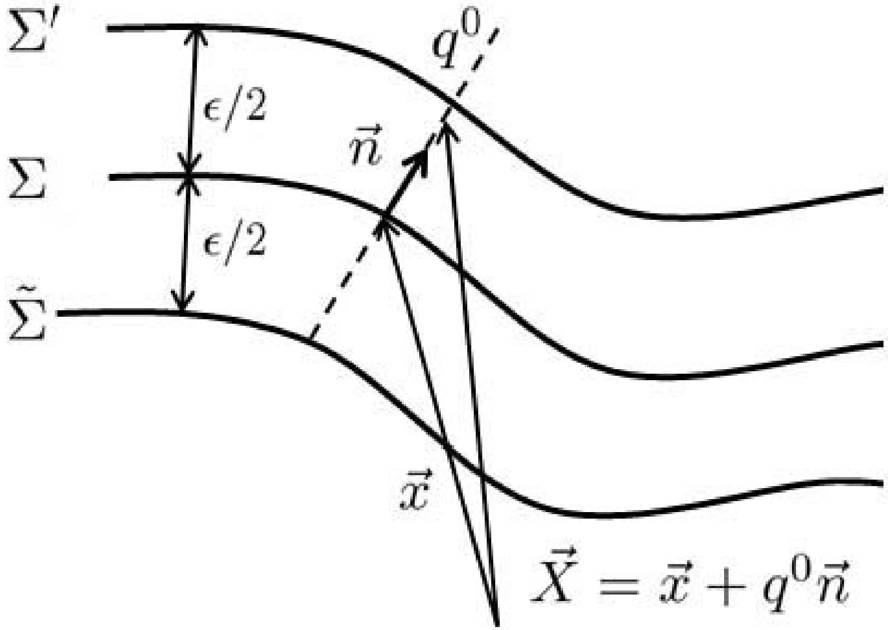
投稿中のため割愛します。

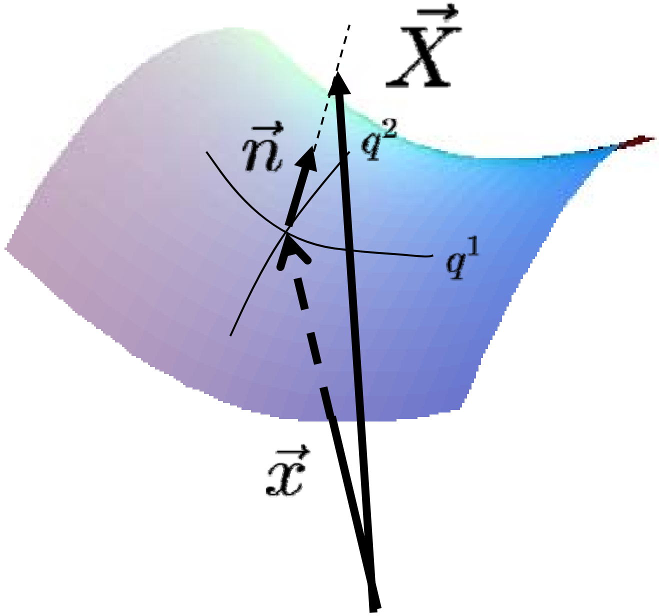
まとめ

- 太さの変化するチューブ内の１次元有効拡散
  → ＦＪ方程式＋有効拡散係数

- 曲線状のチューブ内の１次元有効拡散
  → 断面内の分布モードごとに異なる
  有効拡散係数を持った拡散方程式

４．曲面に挟まれた空間での拡散





$$\vec{X}(q^0, q^1, q^2) = \vec{x}(q^1, q^2) + q^0\vec{n}$$

$$-\epsilon/2 \leq q^0 \leq \epsilon/2$$

Metric neighborhood of surface

$$G_{\mu\nu} = \frac{\partial \vec{X}}{\partial q^\mu} \cdot \frac{\partial \vec{X}}{\partial q^\nu}$$

$$\begin{aligned} G_{ij} = g_{ij} + q^0 \Big(\frac{\partial \vec{x}}{\partial q^i} \cdot \frac{\partial \vec{n}}{\partial q^j} + \frac{\partial \vec{x}}{\partial q^j} \cdot \frac{\partial \vec{n}}{\partial q^i} \Big) \\ + (q^0)^2 \frac{\partial \vec{n}}{\partial q^i} \cdot \frac{\partial \vec{n}}{\partial q^j} \quad (i, j = 1, 2) \end{aligned}$$

$$g_{ij} = \vec{B}_i \cdot \vec{B}_j .$$

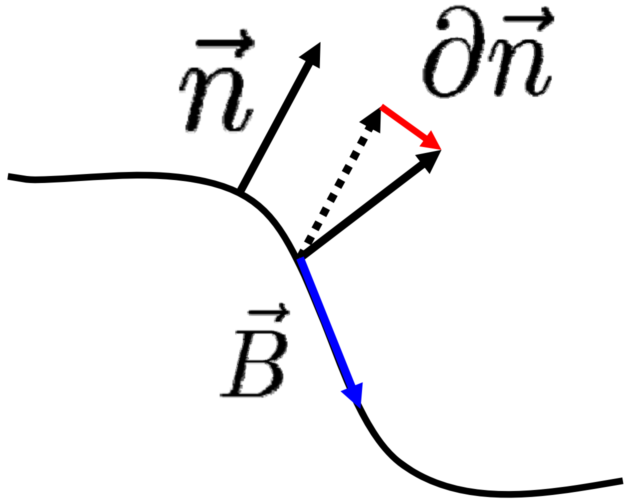
$$G_{0i} = G_{i0} = 0, \quad G_{00} = 1.$$

曲面の曲率

第2基本計量

$$\kappa_{ij} = \frac{\partial \vec{n}}{\partial q^i} \cdot \vec{B}_j.$$

$$g_{ij} = \vec{B}_i \cdot \vec{B}_j$$



$$\vec{B}_k = \frac{\partial \vec{x}}{\partial q^k}$$

Tangential vector

Tools for geometrical study

Gauss equation

$$\frac{\partial \vec{B}_i}{\partial q^j} = -\kappa_{ij}\vec{n} + \Gamma^k_{ij}\vec{B}_k,$$

Weingarten equation

$$\frac{\partial \vec{n}}{\partial q^j} = \kappa^m_j \vec{B}_m$$

Second Fundamental Tensor $\kappa_{ij} = \frac{\partial \vec{n}}{\partial q^i} \cdot \vec{B}_j.$

Mean Curvature **Ricci Scalar, Gauss Curvature**

$$\kappa = g^{ij}\kappa_{ij}, \quad R/2 = det(g^{ik}\kappa_{kj}) = det(\kappa^i_j).$$

Form of metric with Curvature

$$G_{ij} = g_{ij} + 2q^0\kappa_{ij} + (q^0)^2\kappa_{im}\kappa_j^m.$$

$$G_{\mu\nu} = \begin{pmatrix} 1 & 0 \\ 0 & G_{ij} \end{pmatrix}.$$

$$G_{ij} = (g_i^m + q^0\kappa_i^m)(g_{mj} + q^0\kappa_{mj}) \sim (g + q^0\kappa)^2$$

Embedding of Diffusion Field

$$\frac{\partial \phi^{(3)}}{\partial t} = D\Delta^{(3)}\phi^{(3)}, \quad 1 = \int \phi^{(3)}(q^0, q^1, q^2)\sqrt{G}\; d^3q$$

$$\downarrow$$

$$\frac{\partial \phi^{(2)}}{\partial t} = D\tilde{\Delta}^{(2)}\phi^{(2)}, \quad 1 = \int \phi^{(2)}(q^1, q^2)\sqrt{g}\; d^2q$$

$$1 = \int \phi^{(3)}(q^0, q^1, q^2)\sqrt{G}\; d^3q \qquad \tilde{\phi}^{(3)}$$

$$= \int [\int_{-\epsilon/2}^{\epsilon/2} dq^0 (\phi^{(3)}\sqrt{G/g})]\; \sqrt{g}\; d^2q$$

$$= \int \phi^{(2)}(q^1, q^2)\sqrt{g}\; d^2q$$

$$\phi^{(2)}(q^1, q^2) = \int_{-\epsilon/2}^{\epsilon/2} \tilde{\phi}^{(3)} dq^0,$$

We multiply $\sqrt{G/g}$ and integrate by q^0 to equation $\dfrac{\partial \phi^{(3)}}{\partial t} = D\Delta^{(3)}\phi^{(3)}$

$$\frac{\partial \phi^{(2)}}{\partial t} = D \int_{-\epsilon/2}^{\epsilon/2} \tilde{\Delta}^{(3)} \tilde{\phi}^{(3)} dq^0$$

$$\tilde{\Delta}^{(3)} \equiv \sqrt{G/g}\ \ \Delta^{(3)} \sqrt{g/G}.$$

$$\tilde{\Delta}^{(3)} = g^{-1/2} \frac{\partial}{\partial q^\mu} G^{1/2} G^{\mu\nu} \frac{\partial}{\partial q^\nu} (g/G)^{1/2} = \tilde{\Delta}^{(2)} + \tilde{\Delta}^{(1)}.$$

$$\tilde{\Delta}^{(2)} \equiv g^{-1/2} \frac{\partial}{\partial q^i} G^{1/2} G^{ij} \frac{\partial}{\partial q^j} (g/G)^{1/2}, \quad \tilde{\Delta}^{(1)} \equiv \frac{\partial}{\partial q^0} G^{1/2} \frac{\partial}{\partial q^0} G^{-1/2}.$$

Boundary Condition

$$\begin{aligned}\int_{-\epsilon/2}^{\epsilon/2} \tilde{\Delta}^{(1)} \tilde{\phi}^{(3)} dq^0 &= g^{-1/2} \int_{-\epsilon/2}^{\epsilon/2} \frac{\partial}{\partial q^0} (G)^{1/2} \frac{\partial}{\partial q^0} \phi^{(3)} \ dq^0 \\ &= g^{-1/2} [\ (G)^{1/2} \frac{\partial \phi^{(3)}}{\partial q^0}] \ |_{-\epsilon/2}^{\epsilon/2} = 0.\end{aligned}$$

Main Part

$$\tilde{\Delta}^{(2)} = \Delta^{(2)} + q^0 \hat{A} + (q^0)^2 \hat{B} + \mathcal{O}(\epsilon^3), \tag{1}$$

where,

$$\hat{A} = -g^{-1/2} \frac{\partial}{\partial q^i} g^{1/2} (2\kappa^{ij} \frac{\partial}{\partial q^j} + g^{ij} \frac{\partial \kappa}{\partial q^j}), \tag{2}$$

$$\hat{B} = g^{-1/2} \frac{\partial}{\partial q^i} g^{1/2} (3\kappa^{im} \kappa^j_m \frac{\partial}{\partial q^j} + \frac{1}{2} g^{ij} \frac{\partial(\kappa^2 - R)}{\partial q^j} + 2\kappa^{ij} \frac{\partial \kappa}{\partial q^j}), \tag{3}$$

Equation

$$\frac{\partial \phi^{(2)}}{\partial t} = D\Delta^{(2)}\phi^{(2)} + D\hat{A}\int_{-\epsilon/2}^{\epsilon/2} q^0 \tilde{\phi}^{(3)} dq^0 + D\hat{B}\int_{-\epsilon/2}^{\epsilon/2} (q^0)^2 \tilde{\phi}^{(3)} dq^0 + \mathcal{O}(\epsilon^3).$$

法線方向への
拡散時間はϵ^2/D
観測時間スケール
が十分に長ければ、
この方向は常に平
衡と考えてよい。

Assumption

$$0 = \frac{\partial \phi^{(3)}}{\partial q^0} = g^{1/2}\frac{\partial G^{-1/2}\tilde{\phi}^{(3)}}{\partial q^0}.$$

$\phi^{(2)}(q^1, q^2) = \int_{-\epsilon/2}^{\epsilon/2} \tilde{\phi}^{(3)} dq^0,$

$$\tilde{\phi}^{(3)} = \frac{1}{N}(G/g)^{1/2}\phi^{(2)}(q^1, q^2), \quad N \equiv \int_{-\epsilon/2}^{\epsilon/2} (G/g)^{1/2} dq^0.$$

Expectation value of q^0

$$< f(q^0) > \equiv \frac{1}{N} \int_{-\epsilon/2}^{\epsilon/2} f(q^0)(G/g)^{1/2} dq^0.$$

$$\begin{aligned} N &= \epsilon + \frac{R}{24}\epsilon^3 + \mathcal{O}(\epsilon^5), \\ < q^0 > &= \frac{\kappa\epsilon^2}{12} + \mathcal{O}(\epsilon^4), \\ < (q^0)^2 > &= \frac{\epsilon^2}{12} + \mathcal{O}(\epsilon^4), \end{aligned}$$

Anomalous Diffusion Equation

$$\frac{\partial \phi^{(2)}}{\partial t} = D\Delta^{(2)}\phi^{(2)} + \frac{\epsilon^2}{12} D(\hat{A}\kappa + \hat{B})\phi^{(2)}$$
$$= D\Delta^{(2)}\phi^{(2)} + \tilde{D} g^{-1/2} \frac{\partial}{\partial q^i}\ g^{1/2}\{(3\kappa^{im}\kappa_m^j - 2\kappa\kappa^{ij})\frac{\partial}{\partial q^j} - \frac{1}{2} g^{ij} \frac{\partial R}{\partial q^j}\}\phi^{(2)}$$

$$-\frac{\partial \phi^{(2)}}{\partial t} = \nabla_i (J_N^i + J_A^i) = g^{-1/2} \frac{\partial}{\partial q^j}\ g^{1/2}(J_N^i + J_A^i) \qquad \tilde{D} = \tfrac{\epsilon^2}{12} D$$

Anomalous Diffusion flow

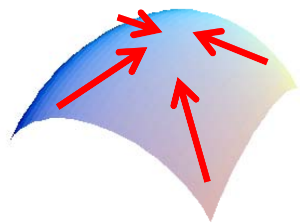
$$J_A^i = -\tilde{D}\{(3\kappa^{im}\kappa_m^j - 2\kappa\kappa^{ij})\frac{\partial \phi^{(2)}}{\partial q^j} - \frac{1}{2} g^{ij} \frac{\partial R}{\partial q^j} \phi^{(2)}\}.$$

Diffusion vs Concentration   curvature gradient flow

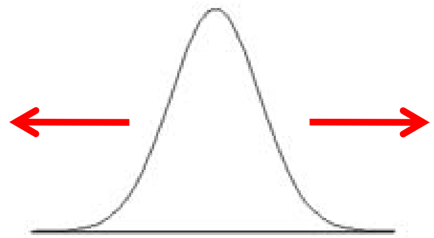
Properties of Anomalous flow

$$J_A^i = -\tilde{D}\{(3\kappa^{im}\kappa_m^j - 2\kappa\kappa^{ij})\frac{\partial\phi^{(2)}}{\partial q^j} - \frac{1}{2}g^{ij}\frac{\partial R}{\partial q^j}\phi^{(2)}\}.$$

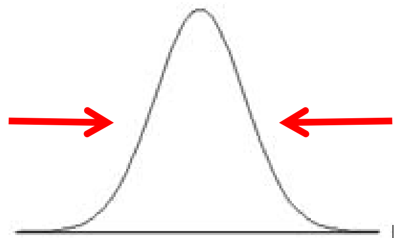
- Ricci Scalar gradient flow
  (From low to higher curvature)



- Diffusion ($f^{ij} \equiv 3\kappa^{im}\kappa_m^j - 2\kappa\kappa^{ij} > 0$)



- Concentration($f^{ij} \equiv 3\kappa^{im}\kappa_m^j - 2\kappa\kappa^{ij} < 0$)



拡散 v.s. 凝集

$$g_{ij} = \delta_{ij}, \quad \kappa^i_j = diag[1/r_1,\ 1/r_2]$$

$$f^{ij} = \delta^{ij}\left(\frac{1}{(r_i)^2} - \frac{2}{r_1 r_2}\right)$$

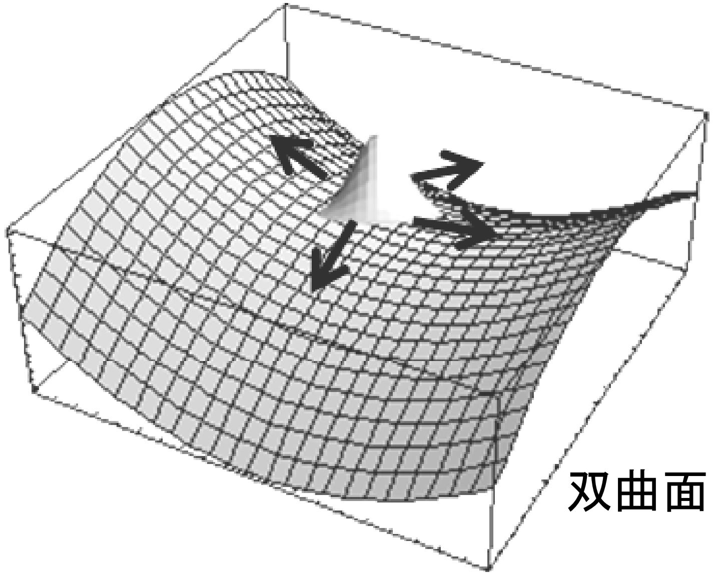
① Hyperbolic Surface（双曲面）R ＜ 0　$f^{11} > 0, \quad f^{22} > 0$　拡散

② Convex-Concave R > 0　$1/2 <| \frac{r_2}{r_1} |< 2.$　$f^{11} < 0, \quad f^{22} < 0$　凝集

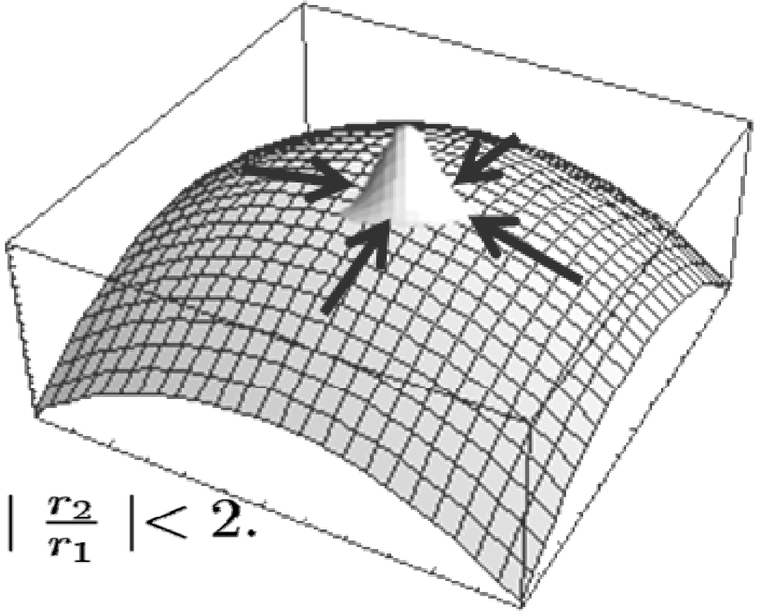
③ Convex-Concave R > 0　$| \frac{r_2}{r_1} |< 1/2, \quad \text{or} \quad | \frac{r_2}{r_1} |> 2.$　$f^{11} f^{22} < 0$　凝集と拡散

④ Flat R ＝ 0　$r_2 = \infty,$　$f^{22} = 0, \quad f^{11} > 0$　一方向拡散

拡散と凝集

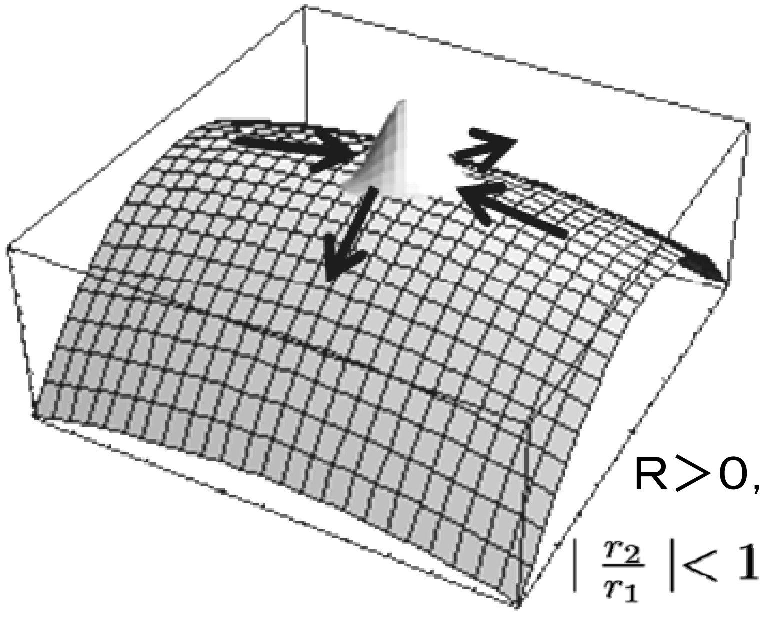


双曲面



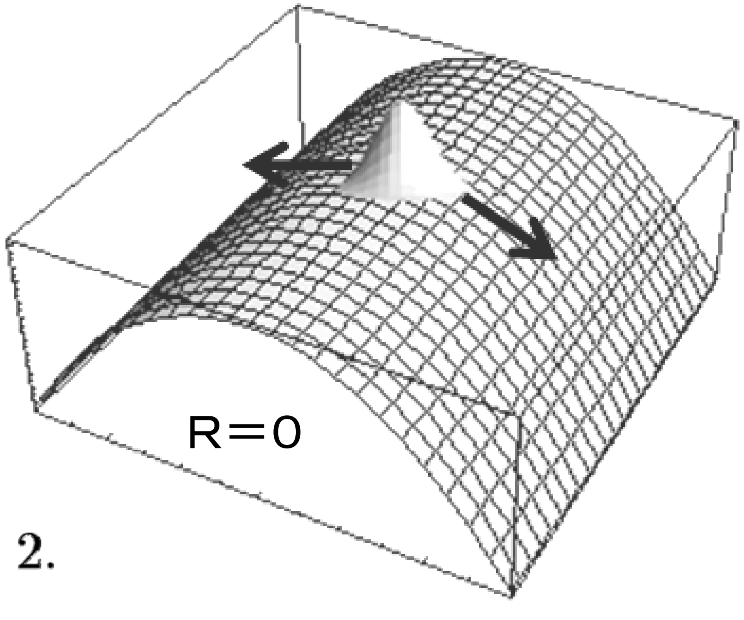
R＞0,

$$1/2 < \left| \frac{r_2}{r_1} \right| < 2.$$



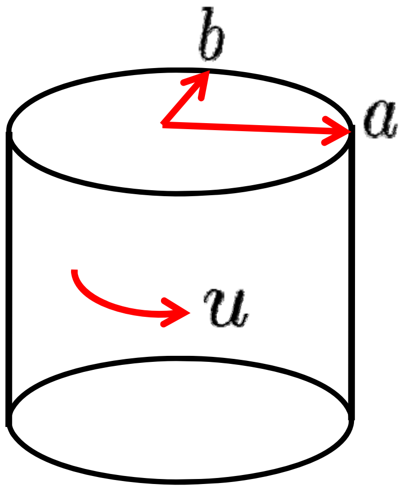
R＞0,

$$\left| \frac{r_2}{r_1} \right| < 1/2, \quad \text{or} \quad \left| \frac{r_2}{r_1} \right| > 2.$$



R＝0

Case of Elliptic Cylinder



$$(\tfrac{x}{a})^2 + (\tfrac{y}{b})^2 = 1$$

$$x = a\cos\theta, \quad y = b\sin\theta.$$

$$f(\theta) \equiv \sqrt{a^2\sin^2\theta + b^2\cos^2\theta}$$

$$du = \sqrt{dx^2 + dy^2} = f(\theta)\ d\theta$$

$$g_{\theta\theta} = f^2, \quad g_{zz} = 1, \quad g_{\theta z} = 0,$$

$$\kappa_{\theta\theta} = \frac{ab}{f}, \quad \kappa_{zz} = \kappa_{\theta z} = 0, \quad \kappa = \frac{ab}{f^3}$$

$$\frac{\partial\phi^{(2)}}{\partial t} = (\frac{1}{f}\frac{\partial}{\partial\theta})D_\theta(\frac{1}{f}\frac{\partial}{\partial\theta})\phi^{(2)} + D\frac{\partial^2}{\partial z^2}\phi^{(2)}$$

Effective Diffusion Coefficient depends on Curvature

$$D_\theta = D(1 + \frac{\epsilon^2\kappa^2}{12}).$$