Modeling Micro Flows: Surface Chemistry, Boltzmann Equation, and Irreversible Thermodynamics

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Rho Shin Myong

Visiting at ASCI FLASH Centre
University of Chicago, U. S. A.
myong@flash.uchicago.edu
and
Permanently at Dept. of Mech. & Aerospace Engr.
Gyeongsang National University, South Korea

Talk Outline

- Modelling issues and fundamental physics in microfluidics
- Gas-surface molecular interaction (boundary condition)
- High order fluid dynamic models (governing equations from BTE)
- Applications
- Concluding remark

Traditional Fluid Dynamics Modelling

- **Linear theory**: Navier-Stokes-Fourier equations
- **Various state-of-art CFD codes:**

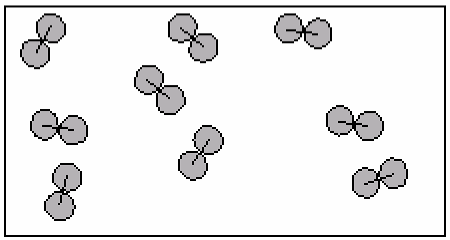
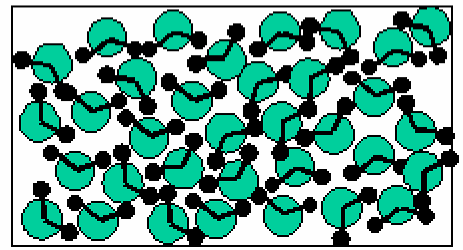
  CFDRC (Aeromechanics, Micro-devices), FLUENT, STAR-CD, ….

  cf. Unsolved problems: turbulence (DNS, LES, …), laminar-turbulent transition, vorticity-dominated flows, …
- Previous major works **in kinetics and irreversible thermodynamics**

Some Example of Microfluidics Study

	USA	EUROPE	JAPAN
Microfluid Connector/valve/ Pump/distributor	- Univ. of Albany - Ohio state Univ.. - UC Berkeley - Univ. of Michigan - Univ. of Utah - UCLA - California Institute of Technology - Defense Medical Research Institute - Lucas Varity Co.	- HSG-IMIT - IMEC - MESA - EPFL - LETI - Fraunhofer - Forschungszentrum Karlsruhe GmbH - Royal Institute of Technology	- Advance Co. - Nagoya Univ.
Micromixer	- Univ. of Hawaii at Manoa - Univ. of Illinois at Urbana Champaign - Stanford Univ.	- Technical Univ. of Denmark	- Mechanical Engineering Lab. - RIKEN
Micro flow controller	- UC Berkeley - UCLA - Intertech Incorporation - Quinn-Curtis Incorporation - Michigan financial Corporation		
Microchip cooler	- UCLA - NASA - JPL - ARC - JSC - MSFC - Univ. of Cincinnati - Case Western Reserve Univ.		
Microcryocooler	- Sienna Tech. Inc. - NASA	- Univ. of Twente	
Microengine	- Dyncorp. - Univ. of Michigan - MIT - UCLA - DARPA - JPL - Caliper technologies corp. - Univ. of Cincinnati - Univ. of California Davis - Case Western Reserve Univ.	- Univ. of Neuchatel	- Instruments Inc. - Univ. of Tokyo
Microgenerator Micromotor	- MIT - UCLA - Maxwell Technologies Inc. - Univ. of Southern California - Georgia Institute of Technology - Case Western Reserve Univ. - Pacific Northwest National Laboratory	- Univ. of South hampton	- Mitsubishi Electric Co. - Seiko Epson Co. - Seiko Instruments inc. - Univ. of Tokyo - Yokohama National Univ.

Gases vs Liquids

Gases (STP)		Liquids	
			
Molecular diameter	0.3 nm	Molecular diameter	0.3 nm
Number density (m^{-3})	3 E25	Number density (m^{-3})	2 E28
Intermolecular spacing	3 nm	Intermolecular spacing	0.4 nm
Displacement distance	100 nm	Displacement distance	1 pm
Molecular Velocity	500 m/s	Molecular Velocity	10^3 m/s

Kn (Knudsen)=mean free path/charac. Length

M (Mach)=velocity/speed of sound

Re (Reynolds)=inertial force/viscous force

Fundamental Questions

- Can the traditional fluids knowledge base be scaled down and applied to microfluidic problems?

  Flow and heat transfer in micro-systems: Is everything different or just smaller? Making things smaller is better approach? (performance)
- Is there any hidden hole which is not obvious in conventional fluid dynamics?
- Role of the 2nd law of thermodynamics:

  Is it simply the umbilical cord? (Finding the most critical element). 2nd law = H-theorem?
- What is the primary parameter to measure the microscale effects? (Kn in liquid?)
- Puzzles

Current Models

- Linear theory: Navier-Stokes
  - suitable for preliminary calculation
  - very efficient and powerful (modern CFD codes)
  - question of applicability
- Molecular description in phase space: Boltzmann equation, DSMC, MD, etc
  - valid for whole flow regimes   cf. DSMC is not applicable to liquid.
  - non-trivial issue in computational efficiency

  cf. Lattice-Boltzmann Method
- High order hydrodynamic theories in thermodynamic space: Chapman-Enskog method (Burnett equation), Grad's moment method, (rational) extended irreversible thermodynamics, information entropy maximization method...
  - achieving economy of thoughts and description
  - problem in non-physical solutions and defining the boundary quantities
- Communities in this area

Boundary Condition

- General comments:

  – universal problem for all theoretical models

  – should describe the molecular interaction of the gas particles with the solid surface (critical in microfluidics.)

  – involves in general the kinetic theory of gases and solid state physics.

- Approaches

  – modify the Boltzmann equation such that the gas-surface interaction manifests itself.

  – based on the scattering kernel (Cercignani-Lampis or Maxwell models)

  – can not tell within the theory how the accommodation coefficient should vary with the type of gas or nature of the wall material.

A Physical Model of Gas–Surface Molecular Interaction

- Theory of gaseous slip based on adsorption:

  Condense on the surface, being held by the field of force of the surface atoms, and subsequently evaporate from the surface

  $\Rightarrow$ time lag $\Rightarrow$ adsorption $\Rightarrow$ slip

- Suppose that we know fraction of molecules reaching equilibrium with the surface α, then slip values become

$$u = \alpha u_w + (1-\alpha)u_r, \quad T = \alpha T_w + (1-\alpha)T_r$$

Langmuir Adsorption Isotherm(1933)

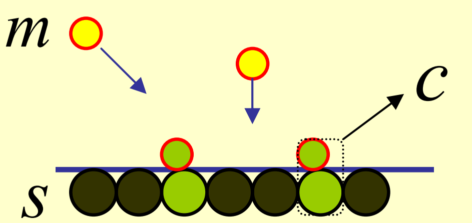
N : number of sites (s) per unit area of the surface interacting with gas molecules (m)

$N\alpha$: number of sites which are covered

$N(1-\alpha)$: number of sites which are not covered

Let us assume that m and s form the complex c. Then the equilibrium constant K becomes

$$K = \frac{C_c}{C_m C_s} = \frac{N\alpha}{\left[p / k_B T_w\right] N(1-\alpha)},$$



that is,

$$\boxed{\alpha = \frac{\beta p}{1+\beta p}} \quad \text{where} \quad \beta = \frac{K}{k_B T_w}.$$

$m + s \Rightarrow c$

Slip Boundary Conditions

- Langmuir slip condition (Dirichlet type)

$$u = \alpha u_w + (1-\alpha)u_r, \quad T = \alpha T_w + (1-\alpha)T_r \ \text{ where } \alpha = \frac{p/4\omega Kn}{1+p/4\omega Kn}$$

$$\omega = \omega_0(\nu)\left(\frac{T_w}{T_r}\right)^{1+2/(\nu-1)} \exp\left(-\frac{D_e}{k_B T_w}\right) = \underline{fn(\nu, T_w, D_e)}$$

D_e : Heat of adsorption [$O(10^{-1} \sim 10)$ kcal/mol]

- Maxwell slip condition (Neumann type)

$$u = u_w + \boxed{\varsigma \Pi_w} = u_w + \sigma_v \ell \left(\frac{\partial u}{\partial n}\right)_w, \quad T = T_w + \sigma_T \frac{1}{\Pr}\frac{2\gamma}{\gamma+1}\ell\left(\frac{\partial T}{\partial n}\right)_w$$

Cf. We can prove $\omega \sim \sigma_v \left(\equiv (2-\theta)/\theta\right)$ in the case of microchannel flow.

As a result, **a physical meaning can be assigned to** $\sigma_{v,T}$.

$$\boxed{\sigma_{v,T} \sim \omega = \omega_0(\nu)\left(\frac{T_w}{T_r}\right)^{1+2/(\nu-1)} \exp\left(-\frac{D_e}{k_B T_w}\right)}$$

High Order Hydrodynamic Models (I)

- Conservation laws: stress and heat flux unknown
- Derivation of the constitutive equations (the moment method)

By differentiating **stress tensor** $\mathbf{P} = \langle m\mathbf{cc}f(\mathbf{v},\mathbf{r},t)\rangle$ with time and combining with the Boltzmann equation $(\partial_t + \mathbf{v}\cdot\nabla) f(\mathbf{v},\mathbf{r},t) = C[f]$,

we obtain $\mathbf{P}_t = -\langle m\mathbf{cc}(\mathbf{v}\cdot\nabla f)\rangle + \mathbf{\Lambda}^{(P)}$ where $\mathbf{\Lambda}^{(P)} \equiv \langle m\mathbf{cc}C[f]\rangle$.

time derivative = kinematics + **dissipation (particle collision)**

$$\mathbf{P}_t = -\nabla\cdot\left[\mathbf{uP} + \boldsymbol{\psi}^{(P)}\right] - \left[\mathbf{P}\cdot\nabla\mathbf{u} + \nabla\mathbf{u}^T\cdot\mathbf{P}\right] + \mathbf{\Lambda}^{(P)}$$

Noting that $\mathbf{P} = p\mathbf{I} + \mathbf{\Pi}$ where $\mathbf{\Pi} \equiv [\mathbf{P}]^{(2)} = \mathbf{P} - \mathbf{I}\,\mathrm{Tr}(\mathbf{P})/3$,

$$\rho\frac{D}{Dt}\left(\frac{\mathbf{\Pi}}{\rho}\right) + \nabla\cdot\boldsymbol{\psi}^{(\Pi)} = -2[\mathbf{\Pi}\cdot\nabla\mathbf{u}]^{(2)} - 2p[\nabla\mathbf{u}]^{(2)} + \mathbf{\Lambda}^{(\Pi)}\left(\equiv\left\langle m[\mathbf{cc}]^{(2)}C[f]\right\rangle\right)$$

➡ Exact: no approximations

Main parameter $\Pi/p \sim \mathrm{Kn}\cdot M$: not Kn alone

No explicit C[f(r,v,t)] except for the dissipation term

Unknown is the stress: not pure hyperbolic

High Order Hydrodynamic Models (II)

- Grad's moment method (1949)

$$\rho \frac{D}{Dt}\left(\frac{\mathbf{\Pi}}{\rho}\right) + \nabla \cdot \boldsymbol{\psi}^{(\Pi)} = -2\left[\mathbf{\Pi} \cdot \nabla \mathbf{u}\right]^{(2)} - 2p\left[\nabla \mathbf{u}\right]^{(2)} + \mathbf{\Lambda}^{(\Pi)} \left(\equiv \left\langle m[\mathbf{cc}]^{(2)} C[f] \right\rangle \overset{Grad}{=} \boxed{-\frac{\mathbf{\Pi}}{\eta / p}} \right)$$

Relaxation (BGK) approximation for C[f] and f in a polynomial form

Closure relation: high order moment $\boldsymbol{\psi}^{(\Pi)}$ ~ heat flux

➡ Mathematical singularity at high Kn**M*

Difficulty in defining moments (stress) at the boundary

- What went wrong?: a simple one-dimensional analysis

$$\frac{\partial \Pi_{xx}}{\partial t} + \Pi_{xx}\left(-\frac{\Pi_{xx_0}}{4\eta/3}\right) + u\frac{\partial \Pi_{xx}}{\partial x} + \left[\nabla \cdot \boldsymbol{\psi}^{(\Pi)}\right]_{xx} = \Pi_{xx}\left(\frac{\Pi_{xx_0}}{\eta}\right) + \frac{\Pi_{xx_0}}{\eta/p} - \frac{\Pi_{xx}}{\eta/p} \text{ where } \Pi_{xx_0} = -\frac{4}{3}\eta\frac{\partial u}{\partial x}$$

➡ Mathematical singularity at $\Pi_{xx_0} = p$

Not removable by different closure or by writing in a pure hyperbolic type

-> require a different calculation of the dissipation term!

High Order Hydrodynamic Models (III)

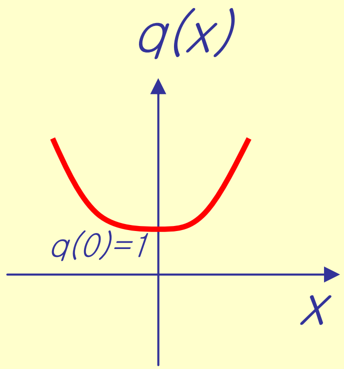
- Eu's modified moment method (1980, 1992, 1998, 2002)

$$\rho \frac{D}{Dt}\left(\frac{\mathbf{\Pi}}{\rho}\right) + \nabla\cdot\boldsymbol{\psi}^{(\Pi)} = -2\left[\mathbf{\Pi}\cdot\nabla\mathbf{u}\right]^{(2)} - 2p\left[\nabla\mathbf{u}\right]^{(2)} + \mathbf{\Lambda}^{(\Pi)}\left(\equiv \left\langle m[\mathbf{cc}]^{(2)} C[f]\right\rangle \overset{Eu}{=} \boxed{-\frac{\mathbf{\Pi}}{\eta/p}q(\kappa)}\right)$$

f in an exponential (not polynomial) form

Cumulant expansion for C[f]

$$\boxed{q(\kappa) \equiv \frac{\sinh\kappa}{\kappa}} \text{ where } \kappa = \frac{(mk_B T)^{1/4}}{\sqrt{2}pd}\left(\frac{\mathbf{\Pi}:\mathbf{\Pi}}{2\eta} + \frac{\mathbf{Q}\cdot\mathbf{Q}}{\lambda}\right)^{1/2}$$



- How it works:

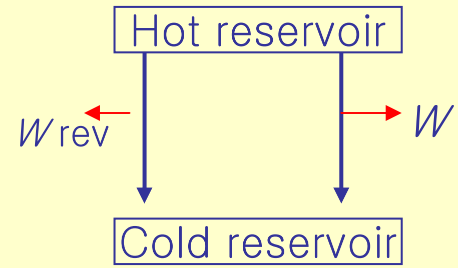
$$0 = \Pi_{xx}\left(\frac{\Pi_{xx_0}}{\eta}\right) + \frac{\Pi_{xx_0}}{\eta/p} - \frac{\Pi_{xx}}{\eta/p}\cdot\left(\frac{\sinh\Pi_{xx}}{\Pi_{xx}}\right)$$

➡ Mathematical singularity can be removed!

Differential -> algebraic equations -> resolve the boundary problem!

Revisit to the 2nd Law of Thermodynamics

$$\eta_{\mathrm{rev}} = \frac{-W_{\mathrm{rev}}}{Q_{\mathrm{H}}} = \frac{Q_{\mathrm{H}} - Q_{\mathrm{C}}}{Q_{\mathrm{H}}} = 1 - \frac{T_{\mathrm{C}}}{T_{\mathrm{H}}}, \quad \eta_{\mathrm{irr}} = \frac{-W}{Q_{\mathrm{H}}} = \frac{Q_{\mathrm{H}} - Q_{\mathrm{C}}}{Q_{\mathrm{H}}} = 1 - \frac{Q_{\mathrm{C}}}{Q_{\mathrm{H}}}$$



By the Carnot theorem $\eta_{\mathrm{rev}} \geq \eta_{\mathrm{irr}}$,

$$-\frac{Q_{\mathrm{C}}}{T_{\mathrm{C}}} + \frac{Q_{\mathrm{H}}}{T_{\mathrm{H}}} \geq 0 \quad \text{Or} \quad -\oint \frac{dQ}{T} \geq 0 \;\; \text{for a series of infinitesimal cycles}$$

Clausius recognized another quantity, the 'uncompensated heat' N

$$N = -\oint \frac{dQ}{T} \geq 0$$

For reversible process

$$\oint \frac{dQ}{T} = 0 = \oint dS_{\mathrm{e}}$$

$dS_{\mathrm{e}} = T^{-1}(dE + dW)$: **equilibrium** Gibbs relation

By realizing dQ : compensated heat exchange to perform the task (work)

N : energy (work) unavailable to the given task

$$N = -\left(\frac{Q_1}{T_1} - \frac{Q_{\mathrm{n}}}{T_{\mathrm{n}}}\right) = -\left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2} + \frac{Q_2}{T_2} - \cdots - \frac{Q_{\mathrm{n}}}{T_{\mathrm{n}}}\right) = -\sum_{j=1}^{n-1} \int_j^{j+1} d\left(\frac{Q}{T}\right) = -\int_1^n \frac{dQ}{T} - \int_1^n Q d\left(\frac{1}{T}\right) \geq 0$$

we can consider N as an independent entity (Eu 2002)

$$\oint dN = -\oint \frac{dQ}{T} \geq 0 \Rightarrow \oint \left(\frac{dQ}{T} + dN\right) = 0 \Rightarrow \oint d\Psi = 0 \;\; \text{where } \Psi \text{ is nonequil. entropy}$$

$d\Psi = T^{-1}(dE + dW) + dN$: extended **nonequilibrium** Gibbs relation

Summary of New Theory

- The nonequilibrium Gibbs relation and entropy imply a special form of the distribution function, exponential.

cf. $\sigma_{ent} = -k_B \langle \ln f \, C[f] \rangle$

Gibbs (information) entropy on $f \le$ Clausius (thermodynamic) entropy on macrostate

- Measure of non-equilibrium in thermodynamic space
  = viscous stress/pressure $\sim \mathrm{Kn} \cdot M \;\sim\; M^2 / \mathrm{Re} = \dfrac{\eta u}{pL}$

- Characteristics
- Complicated nonlinear coupling
- Smaller stress compared with linear theory => slip

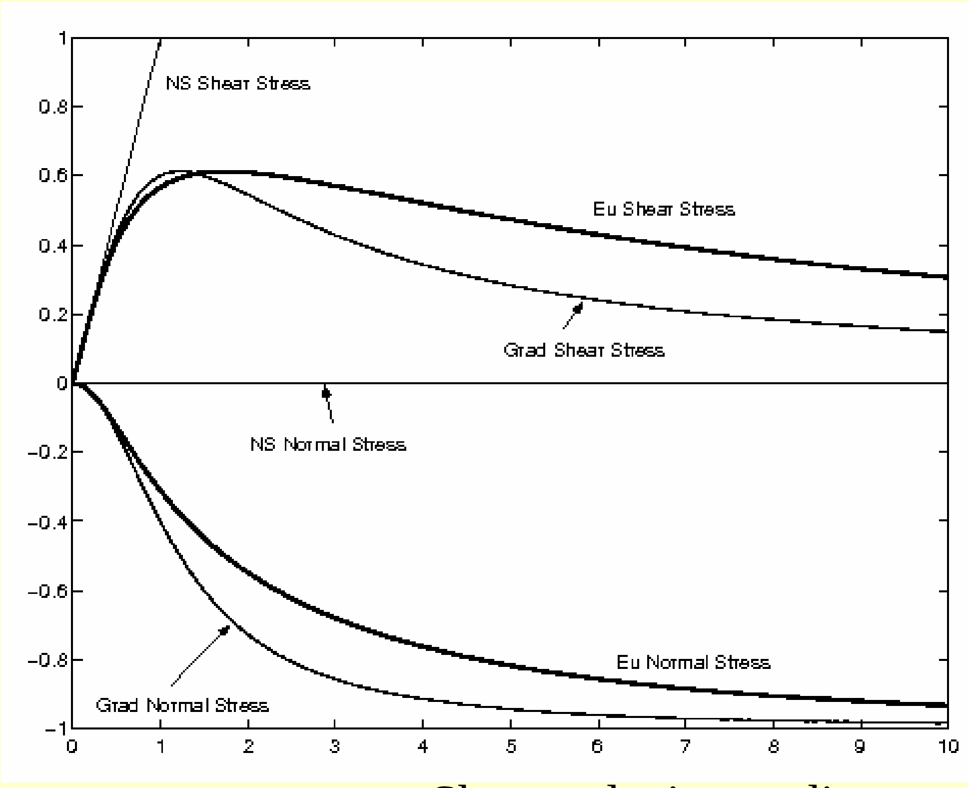
- Key problems
  1) Shock wave and expanding gas
  2) Shear flow (shear velocity gradient) ⇦ microfluidics

- Multi-dimensional computations: done in case of high speed gas flows

Description of Slip

- The slip phenomenon consists of two components;
  1) **non-linear and coupling effects in bulk flow** measured by Kn*M
  2) **gas-surface molecular interaction** measured by Kn

Constitutive relations in shear flow



Shear velocity gradient

- Sequence of gaseous slip as Kn*M increases

slip by **gas - surface interaction**

⇓

the **coupling** effect among the normal and shear stresses

⇓

slip by the **nonlinearity** effect of the shear stress

Cf. The dissipation does not have much impact on the shear flow problem.

Validation Study: Velocity Slip in Isothermal Flow

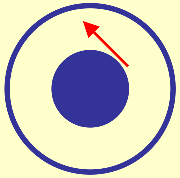
- Verification vs validation (with experiment—always multi-dim.!)
  - Extreme care must be taken to study microfluidics due to difficulty in verification (scaling effects etc).
  - First-order quantities such as velocity profile are not enough to validate the models (ex. drag, heat transfer).
- Pressure-driven compressible flow in microchannel with finite length

$$\frac{\partial(pu)}{\partial x} + \frac{\partial(pv)}{\partial y} = 0, \qquad \frac{dp}{dx} = \frac{\partial^2 u}{\partial y^2} \quad \text{with slip b.c.} \Rightarrow \quad p(x), u(x,y), v(x,y)$$

Ex. Experiment in micro-channel (silicon, $H = 1.2\mu m, W = 40\mu m, L = 4mm$)

$$\mathbf{Kn} \cdot \mathbf{M} \approx \mathbf{O}(\mathbf{10}^{-4}),\ \mathbf{M} \approx \mathbf{O}(\mathbf{10}^{-3}),\ \mathbf{Kn} \approx \mathbf{O}(\mathbf{10}^{-1})$$

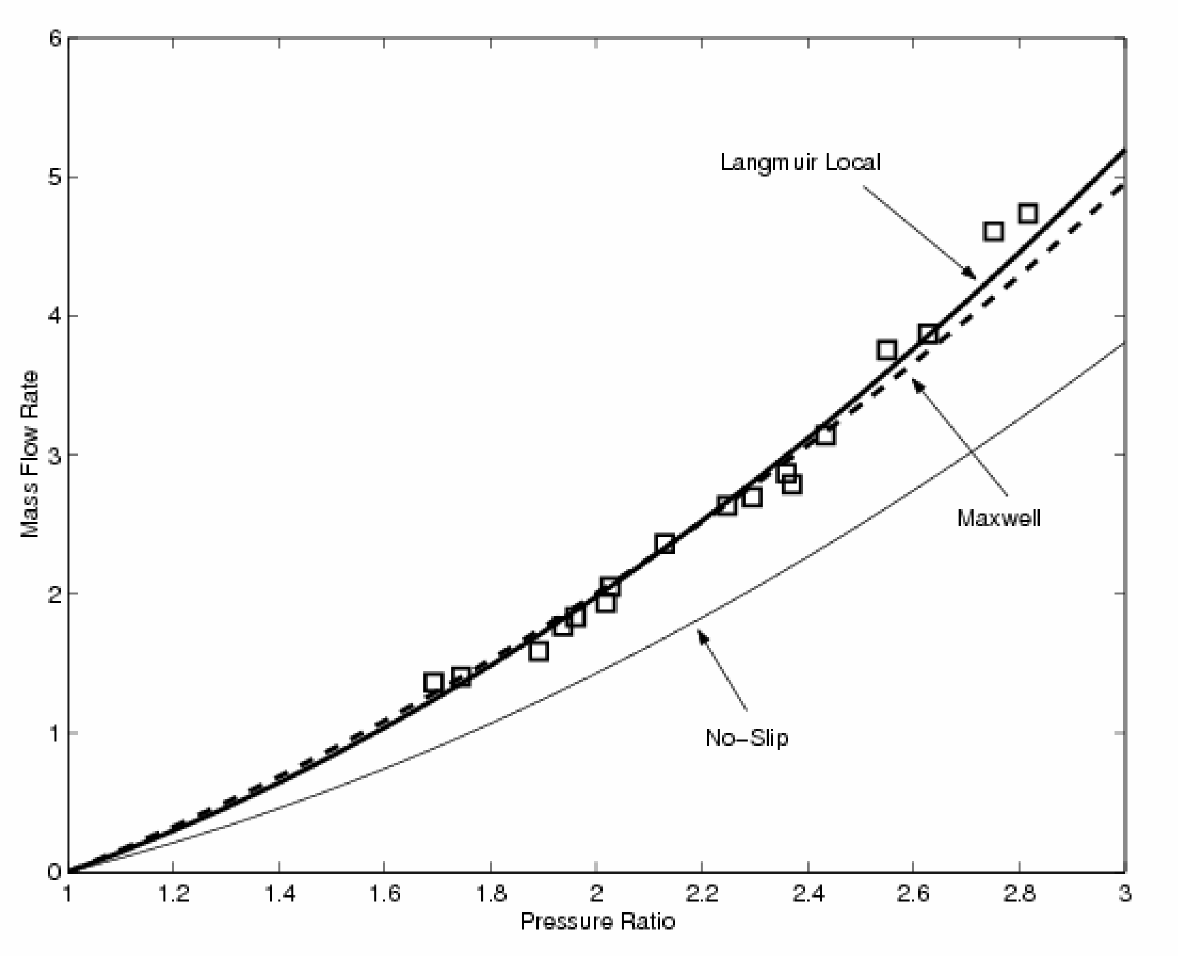
- Microscale cylindrical Couette flow (cylindrical coordinate)



$$\nabla \cdot \mathbf{u} = 0, \qquad \eta \nabla^2 \mathbf{u} = 0 \quad \text{with slip b.c.} \Rightarrow \quad u_\theta(r) \text{ only}$$

$$u_\theta(R_1) \text{ and } u_\theta(R_2)\ ?$$

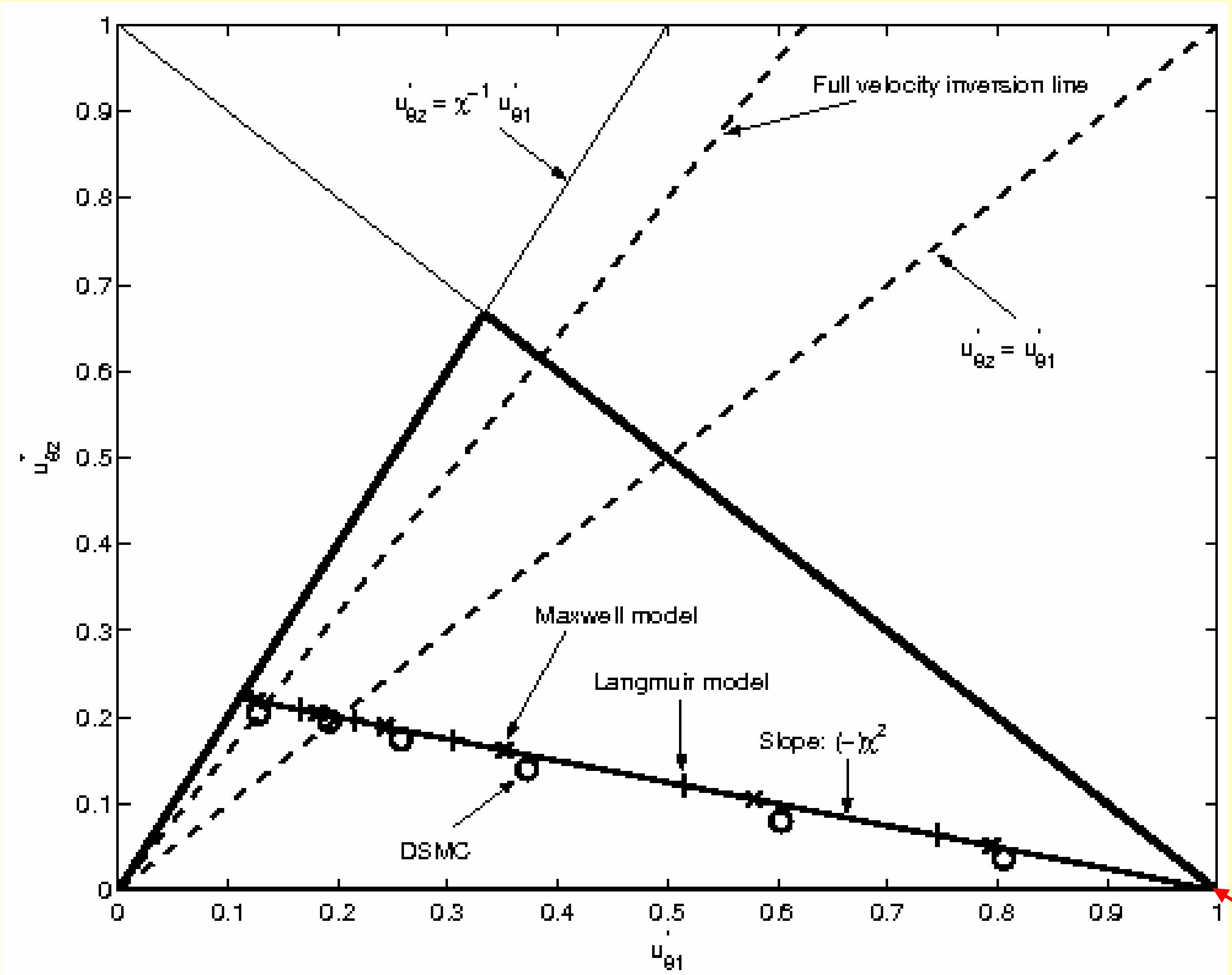
Pressure-Driven Micro-channel Gas Flows (Nitrogen, Kn=0.054)

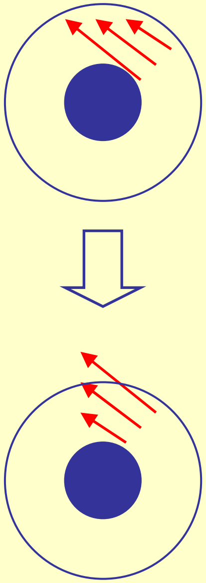


$$\dot{m} = \frac{H^3 W p_{exit}^2}{12\eta LRT} \cdot \left[-\frac{dp}{dx} \right]_{exit} \left(1 + 6\omega \mathrm{Kn} \right)$$

Microscale Cylindrical Couette Gas Flows (Rotating Inner Cylinder, Kn=0.1)

Velocity at the outer cylinder





Continuum limit

Velocity at the inner cylinder

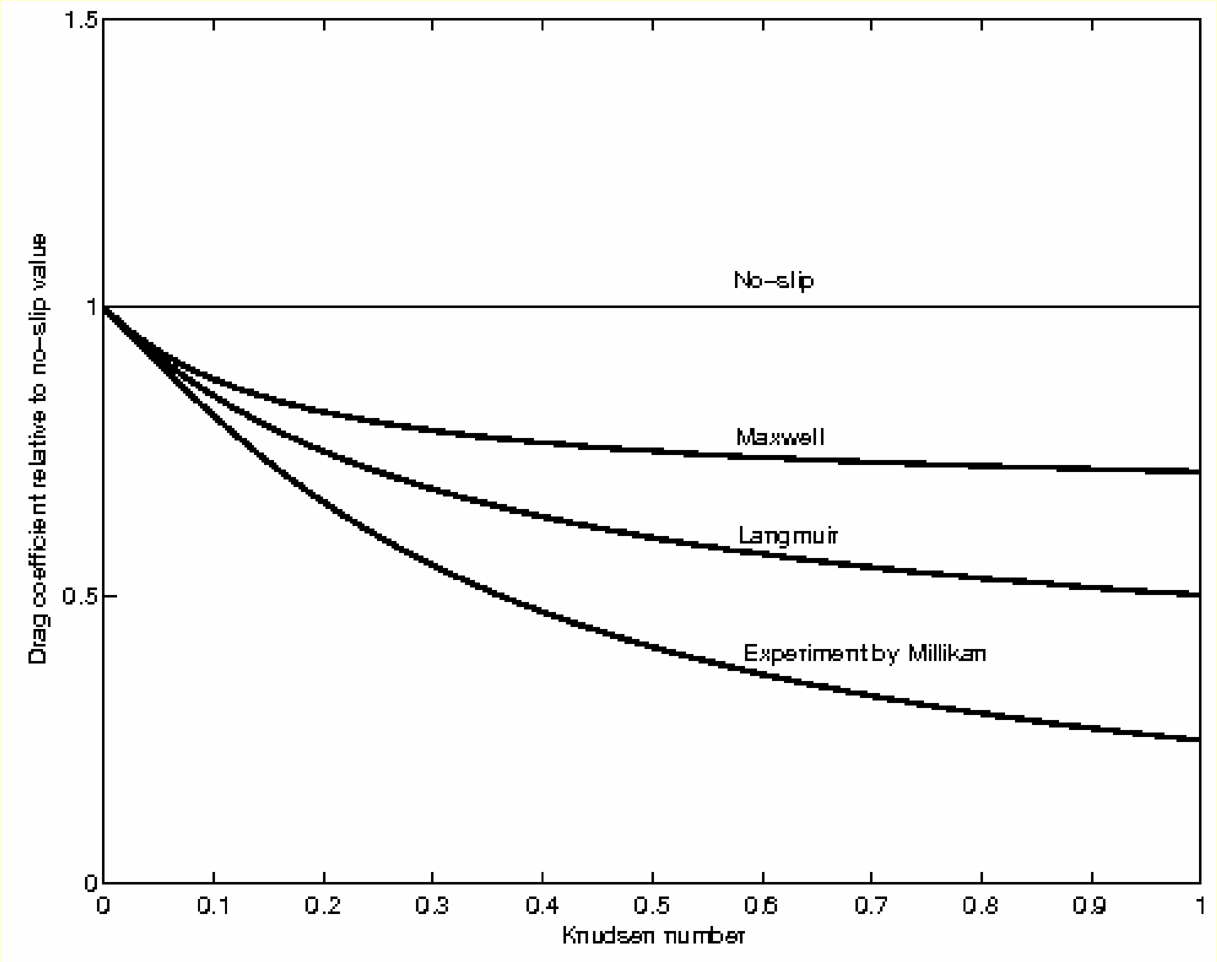
Creeping Gas Flow past a Micro-Sphere (Extended Stokes' Problem)

$$\nabla \cdot \mathbf{u} = 0$$

$$\nabla p = \eta \nabla^2 \mathbf{u}$$

with slip b. c. ⇨ $p, u_r, u_\phi(r, \phi)$

Drag coefficient



Microscale Heat Transfer in Tube Flow

- An extended Graetz problem

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{du}{dr}\right) = \text{constant}$$

$$\rho C_p u \frac{\partial T}{\partial z} = \lambda\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right]$$

with slip b.c. ⇨ $u(r), T(r,z)$

Solution : Non-classical Sturm-Liouville boundary value problem

Involving confluent hypergeometric function (*Mathematica*)

- Reynolds analogy? (heat transfer Nu vs momentum transfer Cf)

$Nu(\text{Nusselt}) \sim C_f \text{Re}$ or $Nu_x \sim \text{Re}_x^n$ (positive n)

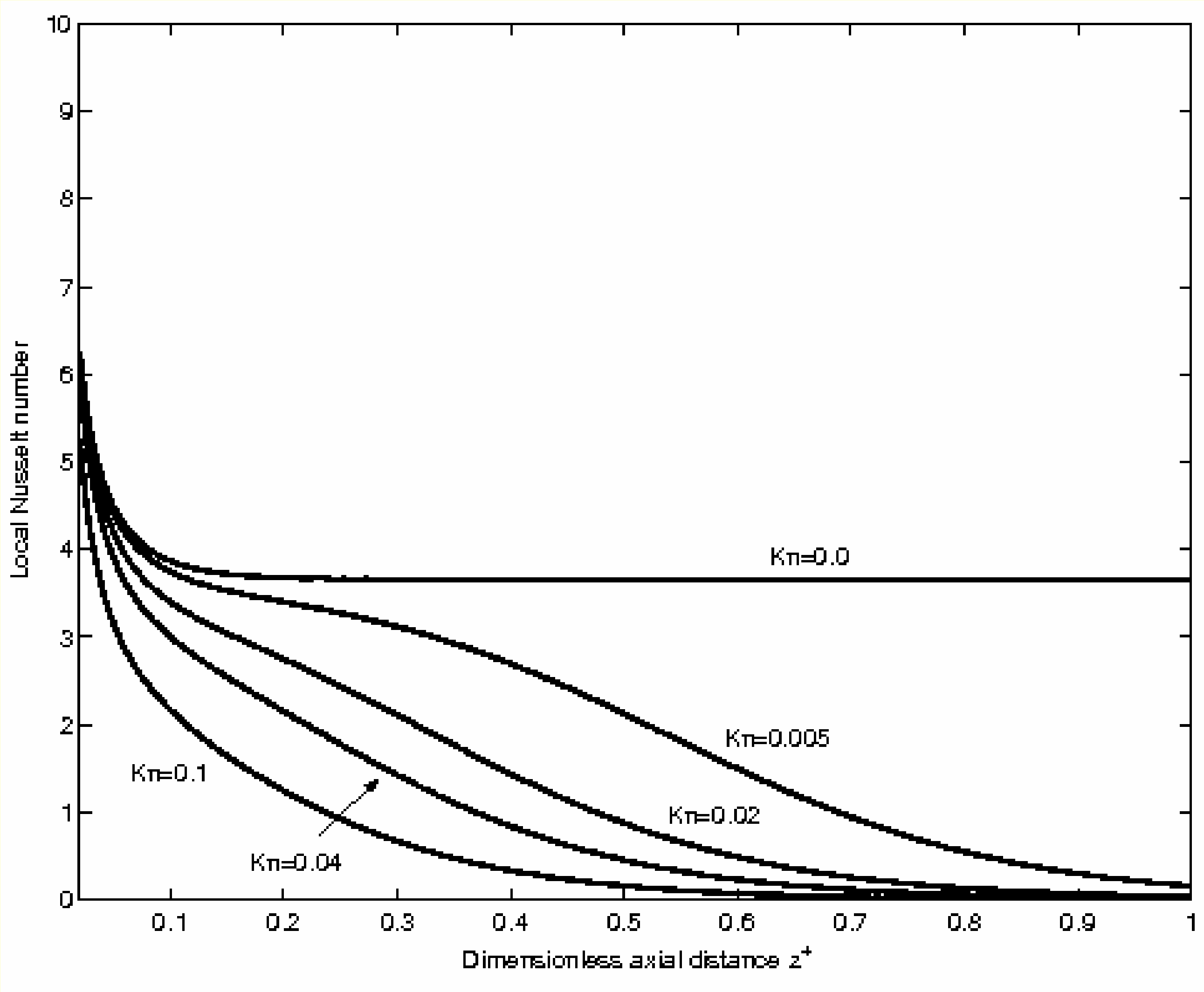
In other words; high Kn $\Rightarrow$ small Re $\Rightarrow$ smaller C_f and Nu

Cf. Maxwell model : Increases if $\sigma_v > \sigma_T$ (violating the Reynolds analogy)

Decreases if $\sigma_v < \sigma_T$

Langmuir model : Always decreases. $\Rightarrow$ **Preserve the Reynolds analogy**

Nusselt Number Profile along Pipe (Pr=2/3, ω=1.0)



New Constitutive Equations

- Conservation laws

$$\begin{pmatrix}\rho \\ \rho\mathbf{u} \\ \rho E\end{pmatrix}_t + \nabla\cdot\begin{pmatrix}\rho\mathbf{u} \\ \rho\mathbf{u}\mathbf{u} + p/\gamma M^2\mathbf{I} \\ \left(\rho E + p/\gamma M^2\right)\mathbf{u}\end{pmatrix} + \frac{1}{\mathrm{Re}}\nabla\cdot\begin{pmatrix}0 \\ \Pi \\ \Pi\cdot\mathbf{u} + \mathbf{Q}/Ec\,\mathrm{Pr}\end{pmatrix} = 0$$

conserved variables: $(\rho, \mathbf{u}, E)$, non-conserved variables: $(\Pi, \mathbf{Q})$

- Generalized hydrodynamics model (monatomic)

$$\hat{\Pi}\, q(c\hat{R}) = \hat{\Pi}_0 + \left[\hat{\Pi}\cdot\nabla\hat{\mathbf{u}}\right]^{(2)}$$
$$\mathbf{Q} q(c\hat{R}) = \hat{\mathbf{Q}}_0 + \hat{\Pi}\cdot\hat{\mathbf{Q}}_0$$

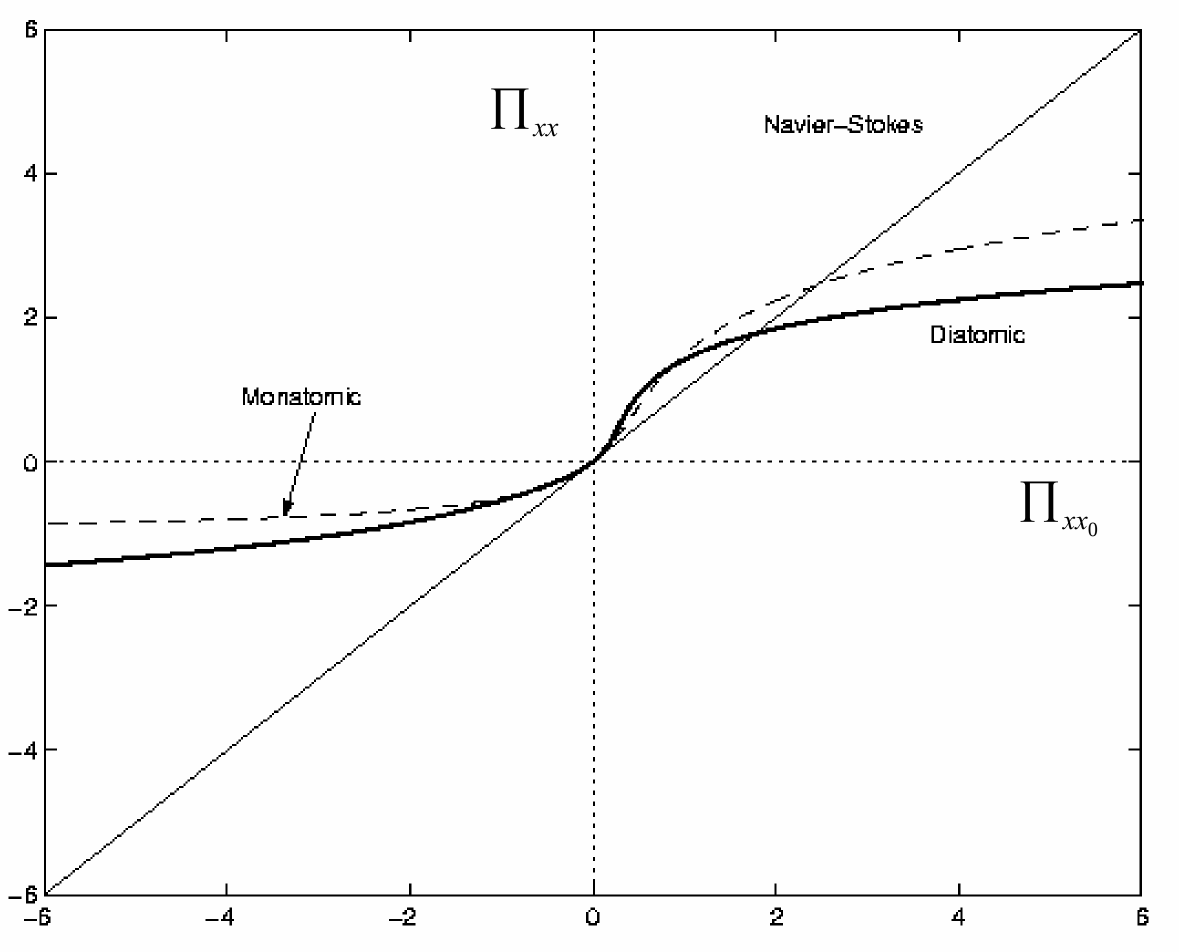
Cf.

$$\Pi_0 = -2\eta\left[\nabla\mathbf{u}\right]^{(2)} \text{ (shear stress tensor)}$$
$$\mathbf{Q}_0 = -\lambda\nabla\ln T \text{ (heat flux)}$$

where $\hat{\Pi} \equiv \frac{N_\delta}{p}\Pi,\ \hat{\mathbf{Q}} \equiv \frac{N_\delta}{p}\frac{\mathbf{Q}}{\sqrt{T/2\varepsilon}},\ \nabla\hat{\mathbf{u}} \equiv \frac{N_\delta}{p}(-2\eta\nabla\mathbf{u}),\ \hat{R}^2 = \hat{\Pi}:\hat{\Pi} + \hat{\mathbf{Q}}\cdot\hat{\mathbf{Q}},\ q(c\hat{R}) = \frac{\sinh(c\hat{R})}{c\hat{R}}.$

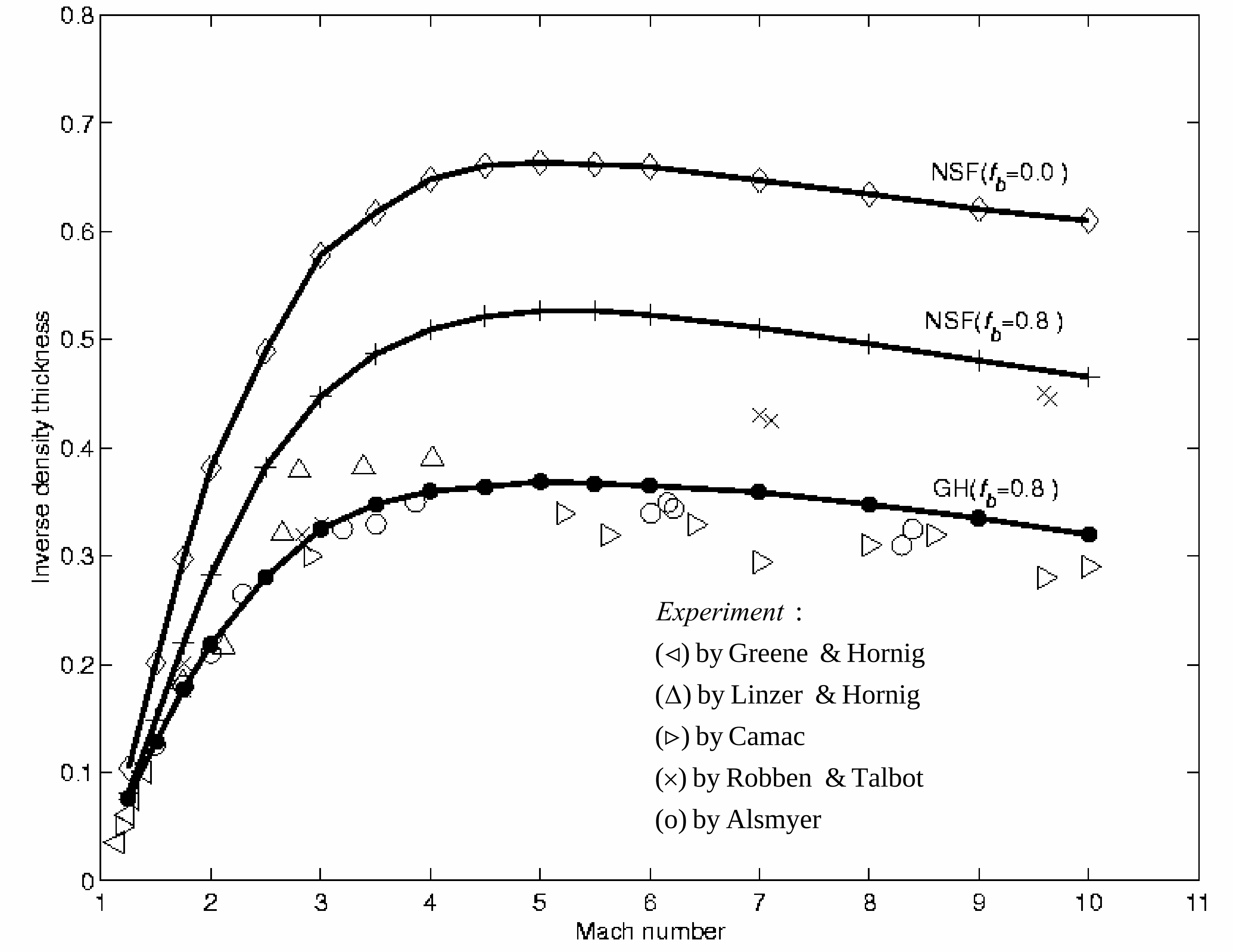
- Algebraic nonlinear but solvable in dimensional splitting by iterative methods: $(\hat{\Pi}, \hat{\mathbf{Q}})$ for known $(\rho, T, \nabla\mathbf{u}, \nabla T)$

Constitutive relation in gas compression and expansion



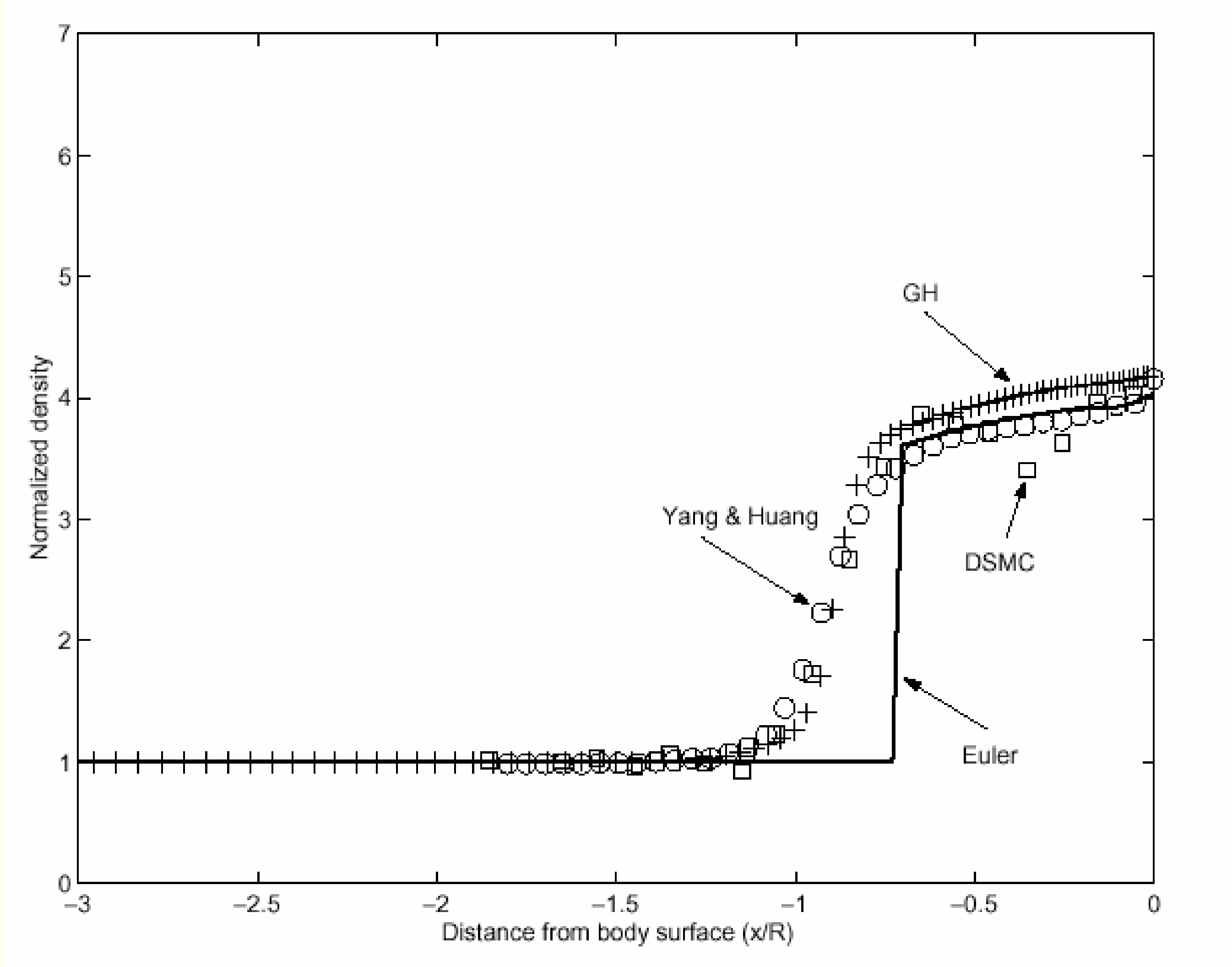
Expansion Compression

Inverse shock density thickness (Nitrogen)



2D Rarefied Hypersonic Flow around a Cylinder

(M=5.48, Kn=0.05, hard sphere)



Density distribution along stagnation streamline

Concluding Remark

- Traditional fluids knowledge base is not enough; gas-surface interaction, coupling and nonlinear effects.
- In microfluidics
  - major parameters Kn*M and Kn (not Kn alone)
  - difficulty in verification and validation
- The connection with phenomenological thermodynamic laws makes the kinetic theory—otherwise, pure mathematical theory—a powerful tool to describe motion of fluids.

  Cf. f(*w*): probability density function of agents with wealth *w* in open market economy

$$f^{Eu} = \exp\left[-\beta\left(\frac{1}{2}mC^2 + \boxed{\sum_k X_k h^{(k)}} - \mu\right)\right] \text{ where } \boxed{\beta \leftarrow \frac{1}{k_B T}}$$

- The extension to other complicated problems, for example, liquid flow, remains to be seen.

  cf. Effective range of momentum transfer owing to a long-range correlation of particles.

Further Subjects

- Implementation of the Langmuir slip model or Maxwell slip model with a slip coefficient correction to CFD codes
- Extension to liquid flow
- Electromagnetic effect and surface tension – MEMS fluid flow
- Quantum effect – charge transport in nano-device