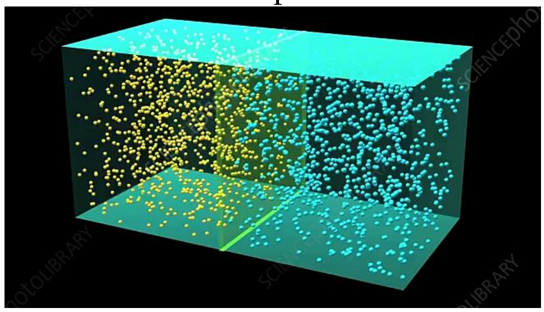
# Molecular Diffusion

- Recall we showed processes like heat conduction and shear stress are due to molecular transport/diffusion
  - due to random motion of molecules and collisions
- Example of mass diffusion after partition raised
  - what is wrong with this simulation?



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- And as molecules move, they carry all their properties with them





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# Diffusion Expressions

- Recall our expressions for diffusion based on $f$
  - **"heat" diffusion** (energy transport in $j$-direction due to random molecular motion)

$$q_j = \int_{-\infty}^{\infty} \left(\frac{1}{2} mC^2\right) nC_j f(C_i) dV_c = \frac{1}{2}\rho \overline{C_j C^2}$$

  - **shear stress** (transverse momentum transport in $j$-direction due to random molecular motion, $i \neq j$)

$$\tau_{ij} = \int_{-\infty}^{\infty} (mC_i) nC_j f(C_i) dV_c = -\rho \overline{C_i C_j}$$

- Now that we have a solution for the velocity distribution $f$ (at equilibrium), we can go back and examine these diffusion terms

# Heat Conduction

- Start with heat conduction $q_j = \frac{1}{2}\rho\overline{C_j C^2}$
  - examine 1st component, $q_1$

$$\frac{q_1}{\rho/2} = \overline{C_1 C^2} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C_1\left(C_1^2 + C_2^2 + C_3^2\right) f(C_i)\, dC_1 dC_2 dC_3$$

  - assuming translational equilibrium $f_o(C_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{-mC^2}{2kT}}$

$$\frac{q_1}{\rho/2} = \overline{C_1 C^2} = \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(C_1 C_1^2 + C_1 C_2^2 + C_1 C_3^2\right) e^{\frac{-m\left(C_1^2 + C_2^2 + C_3^2\right)}{2kT}}\, dC_1 dC_2 dC_3$$

$$\int_{-\infty}^{\infty} odd = 0$$

Odd functions in $C_1$ — Even function in $C_1$

- Therefore $q_1$=0, same for other components

***if in translational equilibrium ⇒ no molecular heat diffusion***







# Shear Stress

- Examine $\tau_{ij}$ ($i \neq j$)

$$\tau_{ij} = -\rho\overline{C_i C_j}$$

  - one component

$$\frac{\tau_{12}}{\rho} = -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C_1 C_2 f(C_i)\, dC_1 dC_2 dC_3$$

$$\frac{\tau_{12}}{\rho} = -\left(\frac{m}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} C_1 e^{\frac{-mC_1^2}{2kT}} dC_1 \int_{-\infty}^{\infty} C_2 e^{\frac{-mC_2^2}{2kT}} dC_2 \int_{-\infty}^{\infty} e^{\frac{-mC_3^2}{2kT}} dC_3$$

Odd — Even

- So $\tau_{12}$=0,
  similar result for all $i \neq j$ terms

***in (translational) equilibrium, no shear stresses***
***– can still have normal stresses (pressure)***

# Diffusion and Nonequilibrium

- Preceding shows that transverse momentum diffusion and diffusion of energy (at least for only $\varepsilon_{tr}$) are **manifestations of translational nonequilibrium**
- "Empirical" models
  - $\tau_{ij} \propto du_i/dx_j$
  - $q_j \propto dT/dx_j$
- *So velocity and temperature gradients must be responsible for (or related to) nonequilibrium velocity distributions*

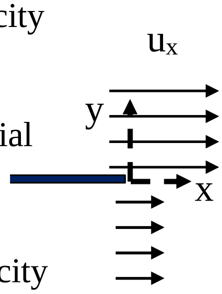




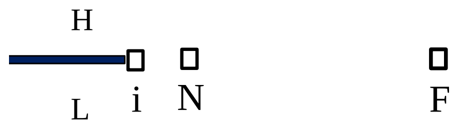


# Shear Stress Example

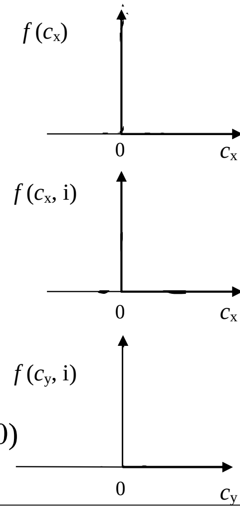
- To understand how velocity gradient leads to shear stress, consider 2-d (subsonic) flow with initial velocity discontinuity




- Examine molecular velocity distribution at three points
  1. Initial (i)
  2. Near field (N)
  3. Far field (F)



# Velocity Distributions: Initial


- Centered volume at initial location contains equal volumes (and numbers) of molecules from H and L fluids
  - same $n$ and $T$, but different mean horizontal velocities ($\bar{c}_x$)
  - subsonic $\Rightarrow \Delta\bar{c}_x < c_{rms}$
- $c_x$ distribution is combination of H and L Maxwellians
- $c_y$ distribution same for both fluids ($\bar{c}_y$=0)
  - same $T \Rightarrow$just shifted version of $c_x$





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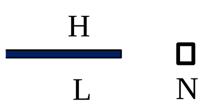
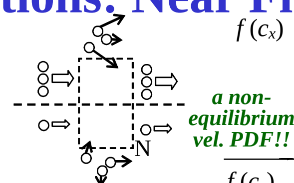
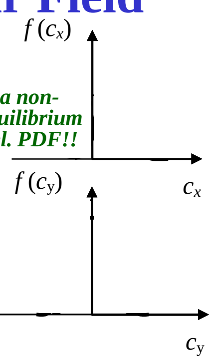
# Velocity Distributions: Near Field

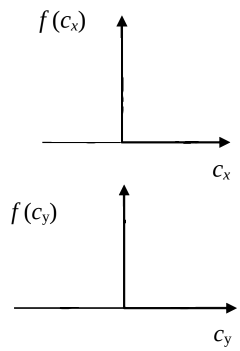



- Molecules convect in from upstream, higher flux in from H, but also higher out
- From above/below, flux in due to $C_y$
  - flux from above has faster $c_x$
- Higher coll. rates for faster molec. (higher $g$)
- $f\,(c_x)$ nonsymmetric, weighted to faster $c_x$ (more influx from H)
  - collisions will move some of fast $c_x$ to lower values
- $f\,(c_y)$ essentially unchanged by fluxes (same in and out)
  - but during collisions some x-momentum is transferred to (random) y-momentum $\Rightarrow f\,(c_y)$ widens *gas gets hotter*!!

## Velocity Distributions: Far Field


- Far downstream, process continues until flow is nearly in equilibrium
  - essentially Maxwellian distributions
  - $f\,(c_x)$ and $f\,(c_y)$ have same widths but different means
- x-momentum from H side has moved toward L side due to $C_y$ (random motion)
  - can call this “**shear stress**” in fluid
- Wider random distribution - hotter
  - can call this “**shear work**” done by fluid





## Boltzmann Equation

- So if we can’t use the equilibrium distribution $f\,(\equiv f_o)$, how can we derive expressions for $\mu$ and $k$, i.e., where do gradient diffusion models come from?
- Approach is to solve the **Boltzmann equation**
  - in its simplest form, it is a transport/conservation eqn. that describes how $f$ at a given $c_i$ can change for a point (small volume element) in a gas due to:
    1. convection of $c_i$ molecules in and out of the volume
    2. body forces (acceleration)
    3. collisions (depleting and replenishing)
  - so it can tell us how the molecular velocity PDF evolves in a non-equilibrium flow

# Chapman-Enskog Solution

- To derive the gradient based diffusion models, we
  1) assume small departures from the equilibrium velocity distribution
     - so $f(c_i)$ close to $f_o(c_i)$ *ends up corresponding to assuming "weak" gradients in the gas*
  2) use a perturbation analysis to find the difference between $f$ and $f_o$, e.g., $f(c_i) = f_o(c_i) + f_o(c_i)\Phi(c_i)$
  3) then with the new $f$, we can find $q_j$ and $\tau_{ij}$
- The result is our familiar gradient models
  - and **expressions for viscosity and thermal conductivity** based on molecular properties
- This approach (with other assumptions) is known as the Chapman-Enskog solution of the Boltzmann equation
  - details in V&K, Chap. X (for monatomic gas)







# Viscosity *T* Dependence

- Recall that our simple hard-sphere model for ideal gas poorly predicted temperature dependence of $\mu$
  - $\mu \propto T^{1/2}$, but should be closer to $T^{0.7}$ for simple gases
- Can we improve without full Chapman-Enskog approach?
- Our simple model for viscosity was $\mu/\rho \propto \lambda\overline{C} = \overline{C}^2/\theta$
  - for near equil, $\overline{C}^2 \propto T$
  - what about using a better model than hard sphere for $\theta$?
- Our general model based on bimolecular collision rate is

$$\theta_{AB} = n_B \int_0^\infty \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^*}{2kT}g^2} \sigma_{AB}^T(g) 4\pi g^3 dg$$

# Viscosity $T$ Dependence: Power Law

- Can improve using our previous power law result for the total collision cross-section $\sigma_{AB}^{T}(g) = a' g^{-4/\alpha}$ ← a constant
- Then $\theta_{AB} = a' n_B \int_0^\infty \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^*}{2kT}g^2} g^{-4/\alpha} 4\pi g^3 dg$
  - can solve using variable substitution $x = \left(\frac{g}{\sqrt{2kT/m_{AB}^*}}\right)$, $dg = \sqrt{2kT/m_{AB}^*}\,dx$

$$\theta_{AB} = a' n_B \left(\sqrt{\frac{2kT}{m_{AB}^*}}\right)^{1-4/\alpha} \underbrace{\int_0^\infty 4\pi^{-1/2} x^{3-4/\alpha} e^{-x^2} dx}_{\text{a constant}}$$

- So

$$\theta_{AB} \propto n_B \left(\sqrt{\frac{2kT}{m_{AB}^*}}\right)^{1-4/\alpha}$$

- Again with $\mu \propto \rho \overline{C}^2/\theta \Rightarrow \mu \propto \cancel{p}T/\cancel{n}\left(T^{1/2-2/\alpha}\right) \propto T^{\frac{\alpha+4}{2\alpha}}$







# Viscosity $T$ Dependence: Power Law

- So $\frac{\mu}{\mu_{ref}} = \left(\frac{T}{T_{ref}}\right)^s \quad s = \frac{\alpha+4}{2\alpha}$ ***same T dep. as C-E with power law***
  *& for hard sphere $\alpha \to \infty$, $s \to 0.5$*
- Compare to gas results (at $T$<100°$C$)

| Gas | $s$ (measured) | α (implied) |
|---|---|---|
| Ne | 0.657 | 12.7 |
| He | 0.685 | 10.8 |
| $N_2$ | 0.756 | 7.81 |
| $O_2$ | 0.814 | 6.37 |
| $CO_2$ | 0.873 | 5.36 |
| $CH_4$ | 0.981 | 4.16 |
| $H_2O$ | 1.10 | 3.33 |

**Intermolecular Potentials**

Ne, He: closer to hard-sphere (very weak attraction)

$N_2$, $O_2$: close to induced+induced dipole (α=6)

$H_2O$: ~dipole-dipole (α=3)

*also: s really s(T); because at high T, less time for attr. forces to act*

# Thermal Conductivity *T* Dependence

- In the absence of internal energy modes (rotation, vibration, electronic), we would find similar results for thermal conductivity, *k*

$$\frac{k}{k_{ref}} = \left(\frac{T}{T_{ref}}\right)^{s}$$

- This is a reasonable approximation for monatomic gases (at not too high *T*)
  - however for other gases, need to include transport of energy carried by molecule's internal energy modes
  - but including internal energy means we also need to consider the effect of **inelastic collisions**