DSMC Simulations of Thermal Gas Separation

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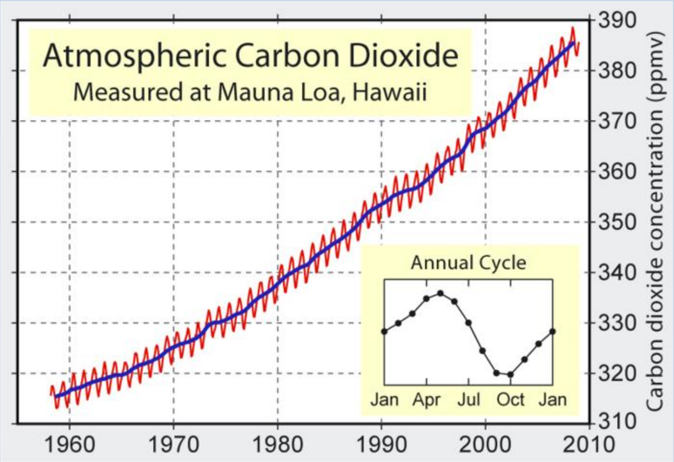
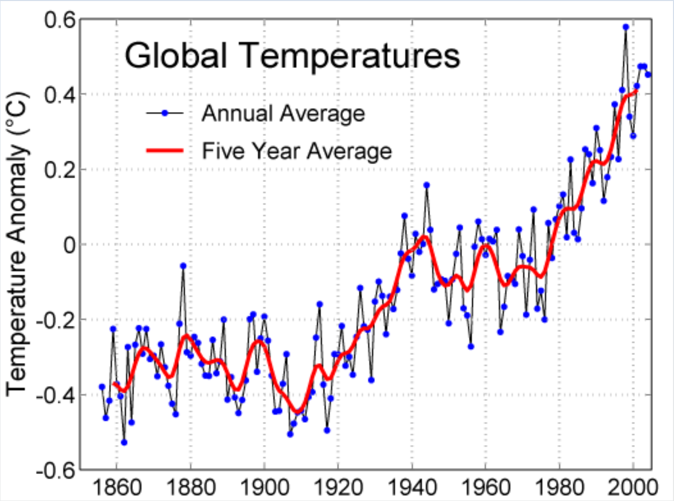
Motivation

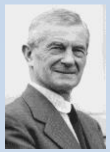
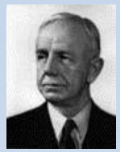
CO_2 levels are rising!





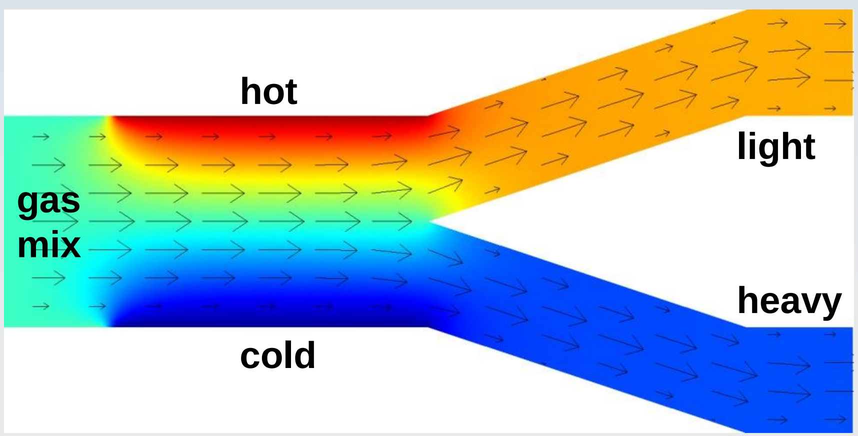
Capture atmospheric CO_2?

Thermal Gas Separation

Sydney Chapman and David Enskog made an amazing discovery 100 years ago.
A temperature gradient in a gas mixture causes its components to separate.

- Light species migrate to hot regions
- Heavy species migrate to cold regions

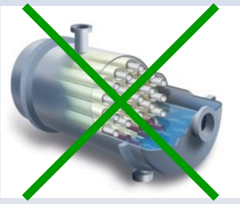


Like heat pump, take advantage of "free" heat ("free" pumping?)


solar energy


no chemicals

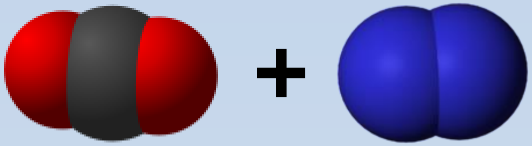

waste heat


no membranes


environmental


no moving parts

Buoyancy-Driven Thermal Separation



Thermal separation is enhanced in a Clusius-Dickel convection column

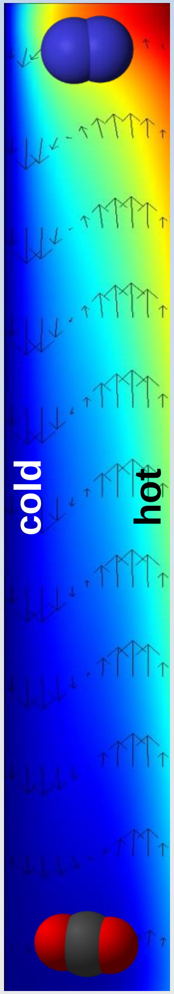
- Long thin vertical column or slot
- One side cold, other side hot
- Counter-current convection flow
- Thermal separation laterally
- Flow-driven separation vertically

Schematic example at right

- Start with 50/50 mixture
- Thermal separation causes 52/48
- Flow carries light up, heavy down
- Final vertical separation 64/36

Problem divides into two parts

- Vertical convection flow
- Lateral thermal separation



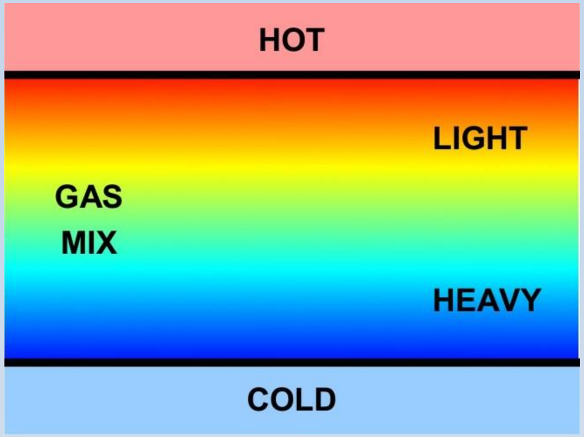
initial		diffuse ∞		convect ∞		average ∞	
cold	hot	cold	hot	cold	hot	cold	hot
50	50	38	34	34	38	36	36
50	50	42	38	38	42	40	40
50	50	46	42	42	46	44	44
50	50	50	46	46	50	48	48
50	50	54	50	50	54	52	52
50	50	58	54	54	58	56	56
50	50	62	58	58	62	60	60
50	50	66	62	62	66	64	64

Steady One-Dimensional Thermal Separation

In general, thermal separation analysis divides into two parts

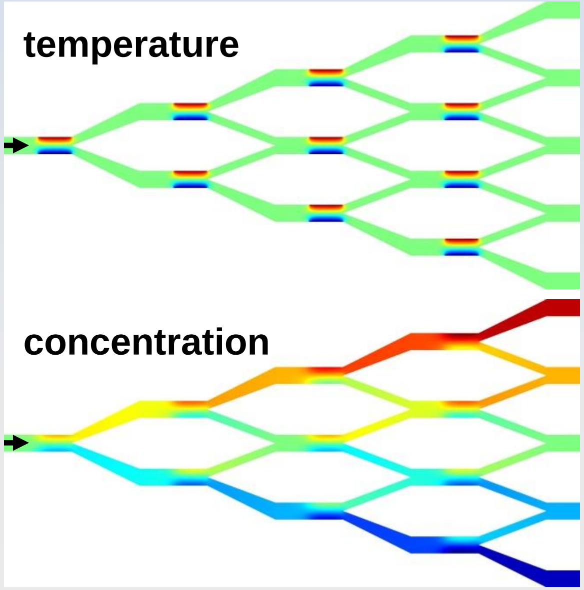
- Free or forced flow used to enhance separation
  - Counter-current buoyant convection in column or slot
  - Co-current forced flow in modular complex plenum
- Thermal separation induced by lateral temperature gradient
  - Dependence on wall-temperature difference
  - Dependence on nominal CO_2 concentration

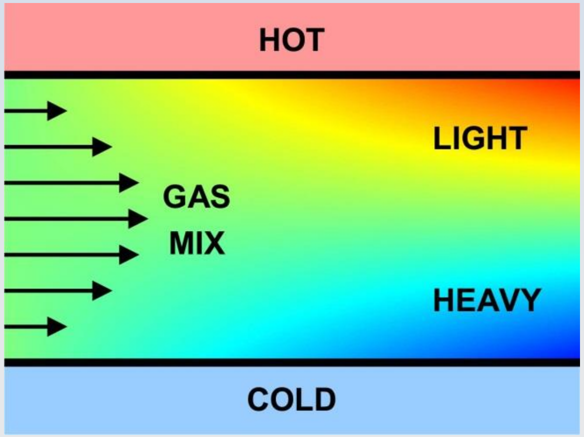
Focus here is on lateral thermal separation



Steady one-dimensional case with no flow (studied here)

Forced flow in a complex geometry (not studied here)





Steady two-dimensional case with flow (not studied here)

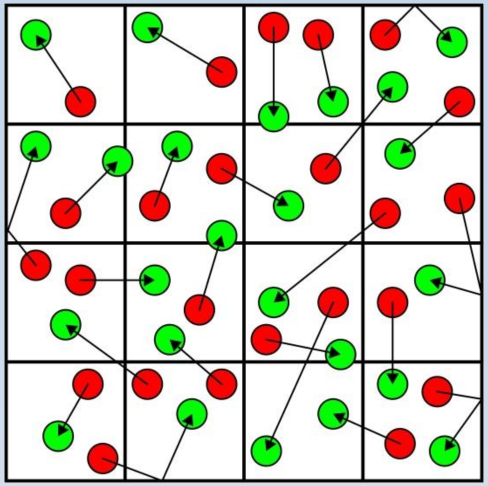
Direct Simulation Monte Carlo (DSMC) Method

Direct Simulation Monte Carlo (DSMC) method uses computational molecules to simulate gas flows (molecular gas dynamics)

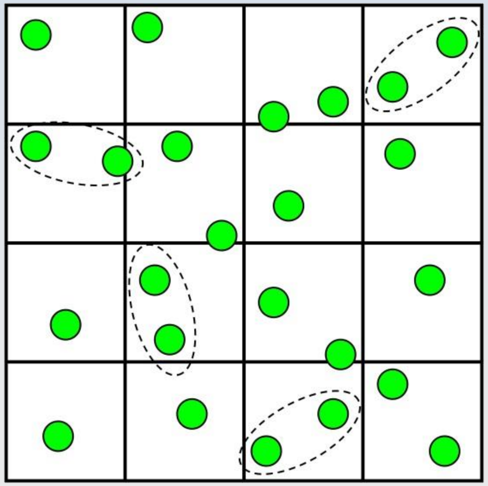
- Computational "simulators" represent many real molecules
  - Can treat multi-component mixtures straightforwardly
- Simulators move ballistically and reflect from walls
  - Walls can be diffuse, specular, or combination
- Simulators collide with each other in a pairwise fashion
  - Collisions yield correct rate and statistics
- Simulator properties are sampled to determine flow properties
  - Number density, velocity, temperature, concentration, etc.

Details of intermolecular potential determine thermal separation

- Maximum for hard-sphere potential ($\omega = 1/2$)
- Zero for Maxwell potential ($F \sim 1/r^5$, $\omega = 1$)
- Intermediate for most molecules ($1/2 < \omega < 1$)
- Accurate molecular models are required

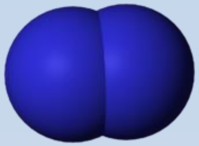


Molecules move



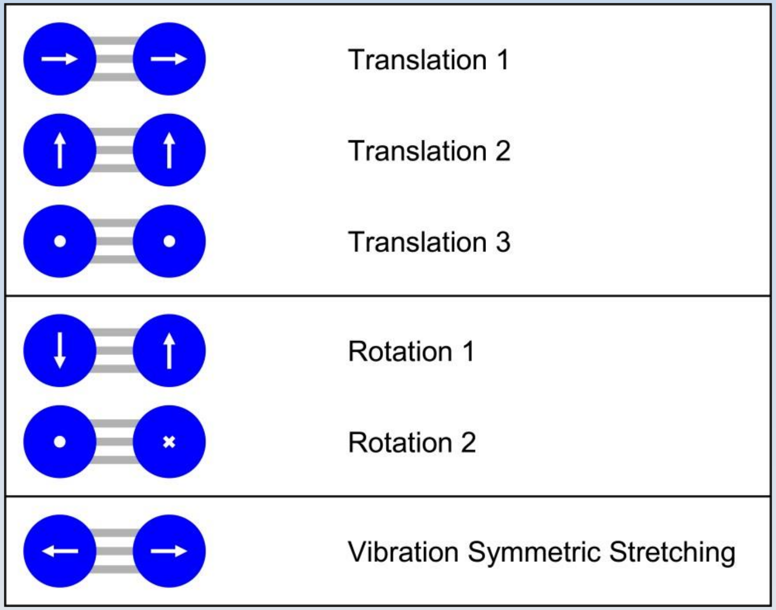
Molecules collide

N_2 Energy Modes and Molecular Model



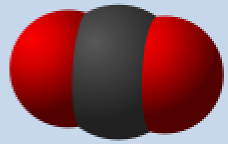
Nitrogen (N_2) molecular model

- Energy modes ($k_BT/2$ each)
  - Translation: 3 modes, fully populated
  - Rotation: 2 modes, fully populated
  - Vibration: 1x2 modes, not fully populated
    - Harmonic Oscillator (HO) model
    - Vibration temperature: 3374.2 K
- Collisions
  - Variable Soft Sphere (VSS) model
  - VSS parameters: Bird (1994)
    - Determine viscosity temperature dependence
    - Values: $\omega = 0.74$, $\alpha = 1.36$
  - Z_{rot} and Z_{vib}: Bird (1994)
    - Inverses of probabilities to exchange rotational and vibrational energy during a collision
    - Values: $Z_{rot} \sim 5$, $Z_{vib} \sim 10^{8\text{-}20}$

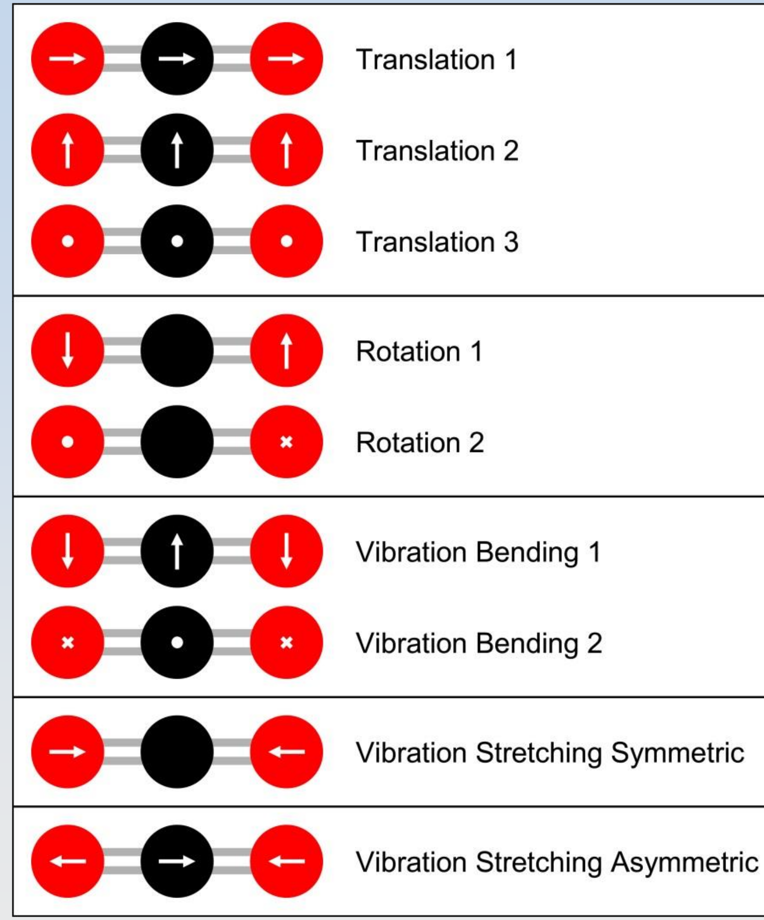


CO_2 Energy Modes and Molecular Model

Carbon dioxide (CO_2) molecular model



- Energy modes ($k_BT/2$ each)
  - Translation: 3 modes, fully populated
  - Rotation: 2 modes, fully populated
  - Vibration: 4x2 modes, not fully populated
    - Harmonic Oscillator (HO) model
    - Vibration temperatures: 945 K (2), 1903 K, 3339 K
- Collisions
  - Variable Soft Sphere (VSS) model
  - VSS parameters: modified Bird (1994)
    - Determine viscosity temperature dependence
    - Values: ω = 0.86 (vs. 0.93), α = 1.54 (vs. 1.61)
  - Z_{rot} and Z_{vib}: Lambert (1977)
    - Inverses of probabilities to exchange rotational and vibrational energy during a collision
    - Values: Z_{rot} = 2.5, Z_{vib} = 5.3
    - Limits: both = 1 or both = ∞



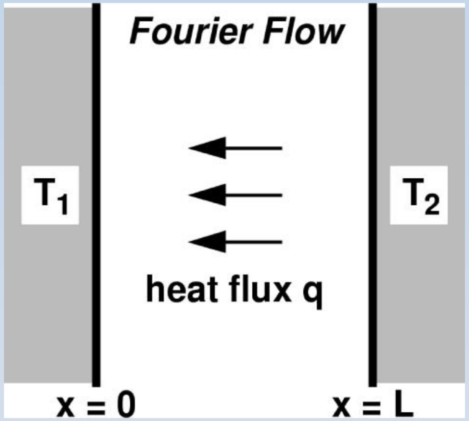
Thermophysical Properties from DSMC Simulations

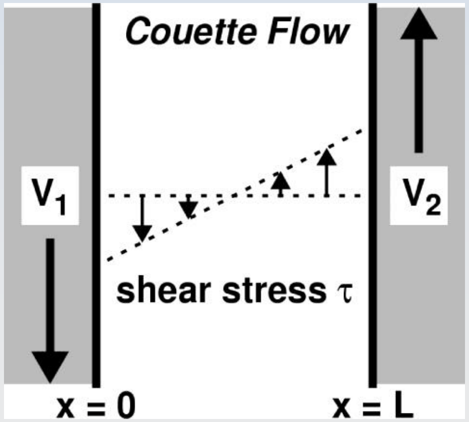
Assess ability of molecular models to reproduce thermophysical properties

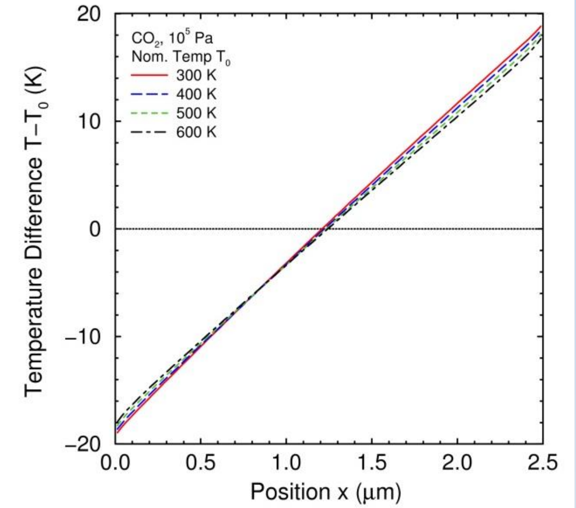
- Both nitrogen and carbon dioxide
- Transport properties
  - Specific heat
  - Viscosity (shear)
  - Thermal conductivity
  - Mass self-conductivity
- Wide temperature range

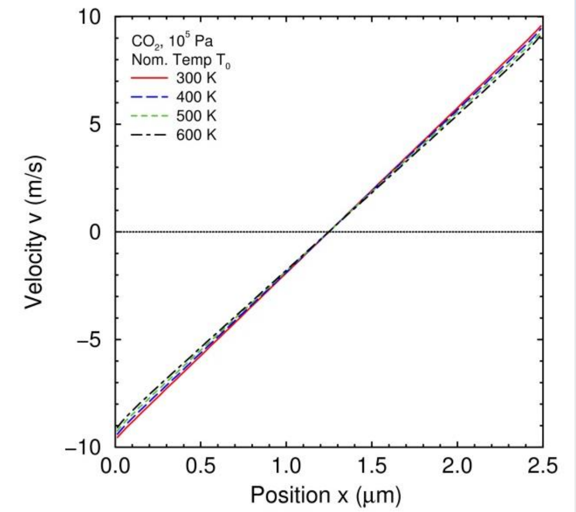
One-dimensional steady flows

- Fourier flow has motionless gas with different-temperature walls
  - Thermal conductivity
  - Specific heat
- Couette flow has same-temperature gas with oppositely sliding walls
  - Viscosity (shear)
  - Mass self-conductivity (inferred)









N_2 Thermophysical Properties from DSMC Simulations

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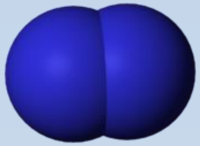
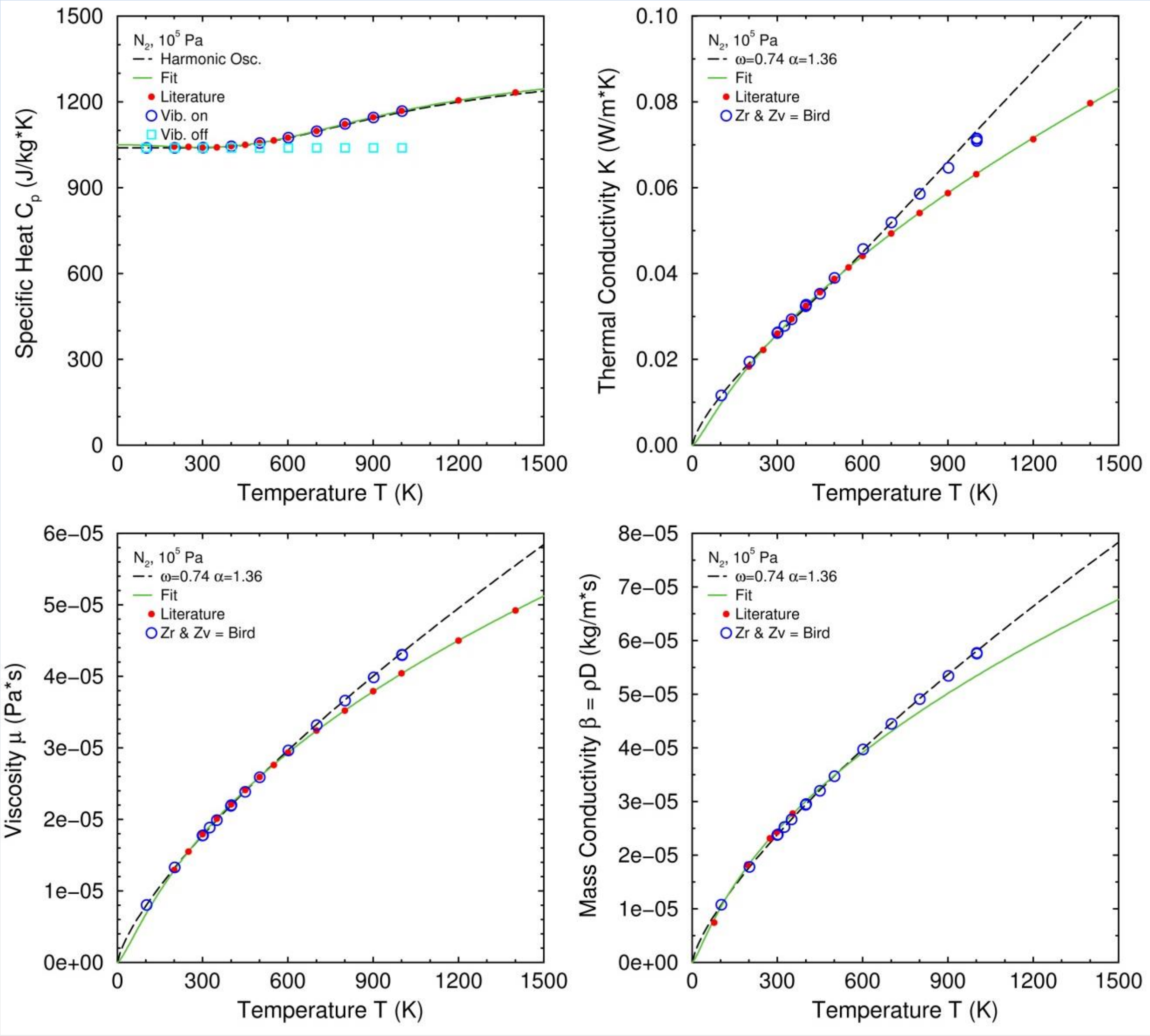


Nitrogen properties

- Specific heat, constant pressure
  - HO model matches experiment
  - Vibration seen above 600 K
- Viscosity, mass conductivity, thermal conductivity
  - VSS model fits experiment fairly well over 300-600 K
  - Significant differences observed above 600 K

Model is good over 300-600 K



CO_2 Thermophysical Properties from DSMC Simulations

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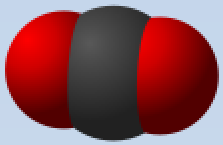
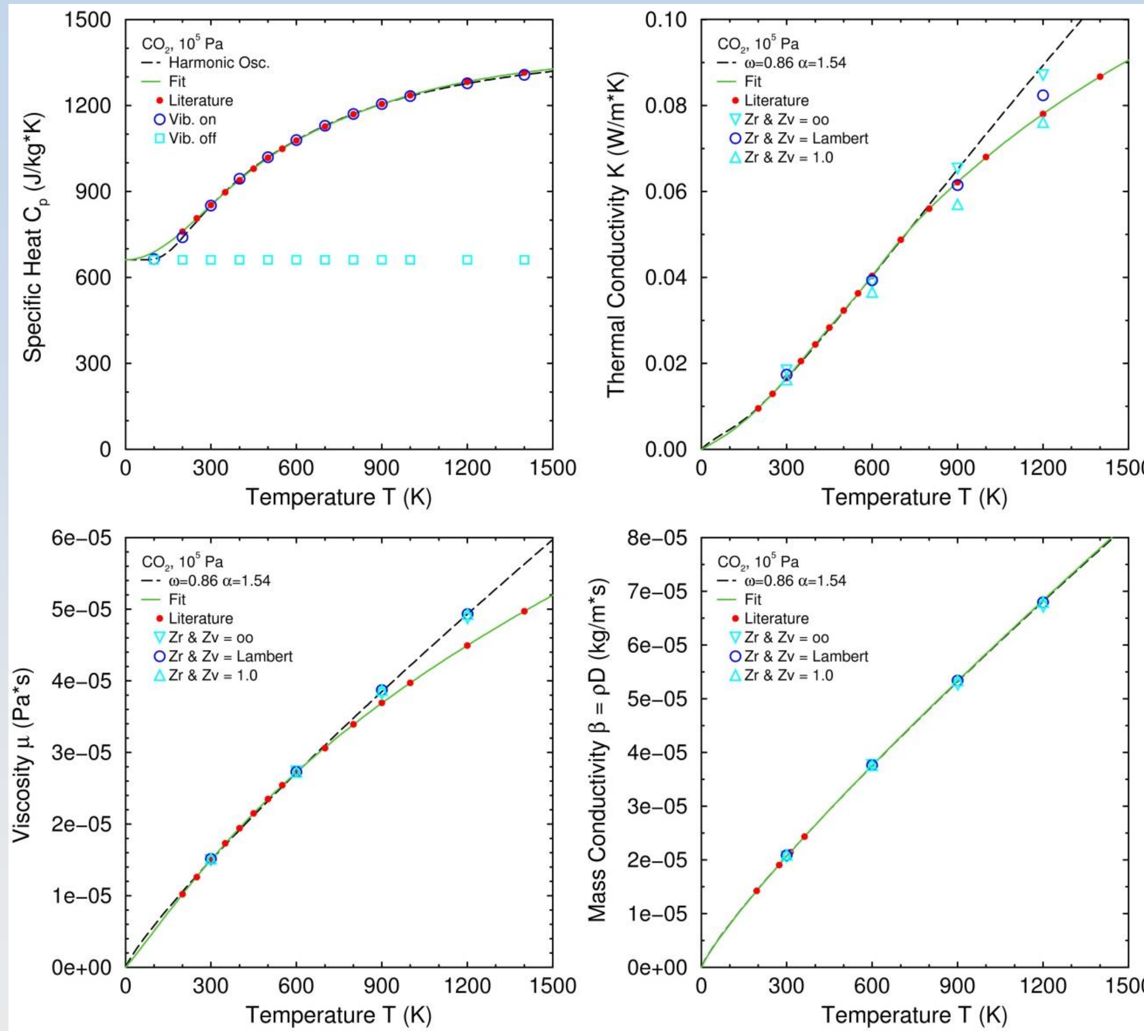


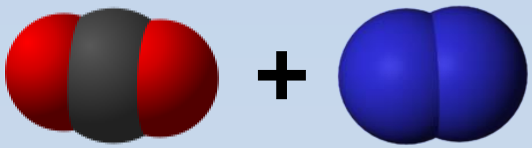
Carbon dioxide properties

- **Specific heat, constant pressure**
  - **HO model matches experiment**
  - **Vibration seen above 100 K**
- **Viscosity, mass conductivity**
  - **VSS model fits experiment fairly well over 300-600 K**
  - **Significant differences observed above 600 K**
  - **Present ω & α fit experiment better than Bird (1994)**
- **Thermal conductivity**
  - **VSS Z_{rot} & Z_{vib} limiting values bound experiment**
  - **VSS Lambert Z_{rot} & Z_{vib} values are close over 300-900 K**

Model is okay over 300-600 K



CO_2-N_2 Temperature Profiles from DSMC Simulations

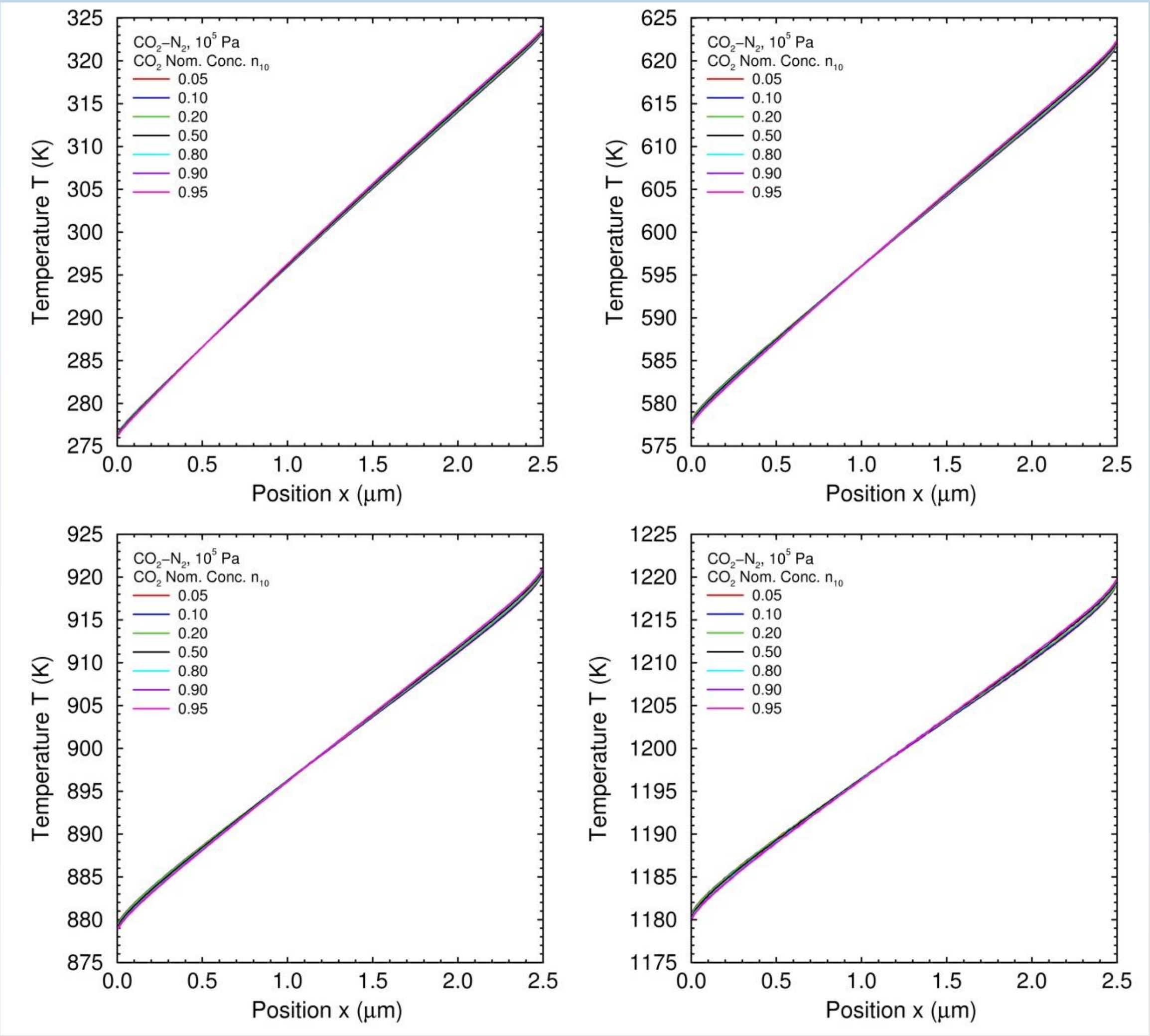


Thermal diffusion simulations

- **CO_2-N_2 mixtures**
- **7 nominal CO_2 concentrations**
  - **5, 10, 20, 50, 80, 90, 95%**
- **4 nominal gas temperatures**
  - **300, 600, 900, 1200 K**
- **Fourier flow – motionless gas with different wall temperatures**
  - **Temperature difference: 50 K**
- **Total of 28 combinations**

All 28 temperature profiles at right

- **Temperature jumps at walls**
- **CO_2 concentration has minimal effect on profile although large effect on heat flux (not shown)**
- **Will need derivative dT/dx**



CO_2 Concentration Profiles from DSMC Simulations

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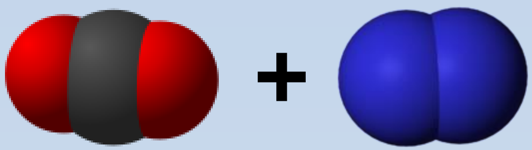
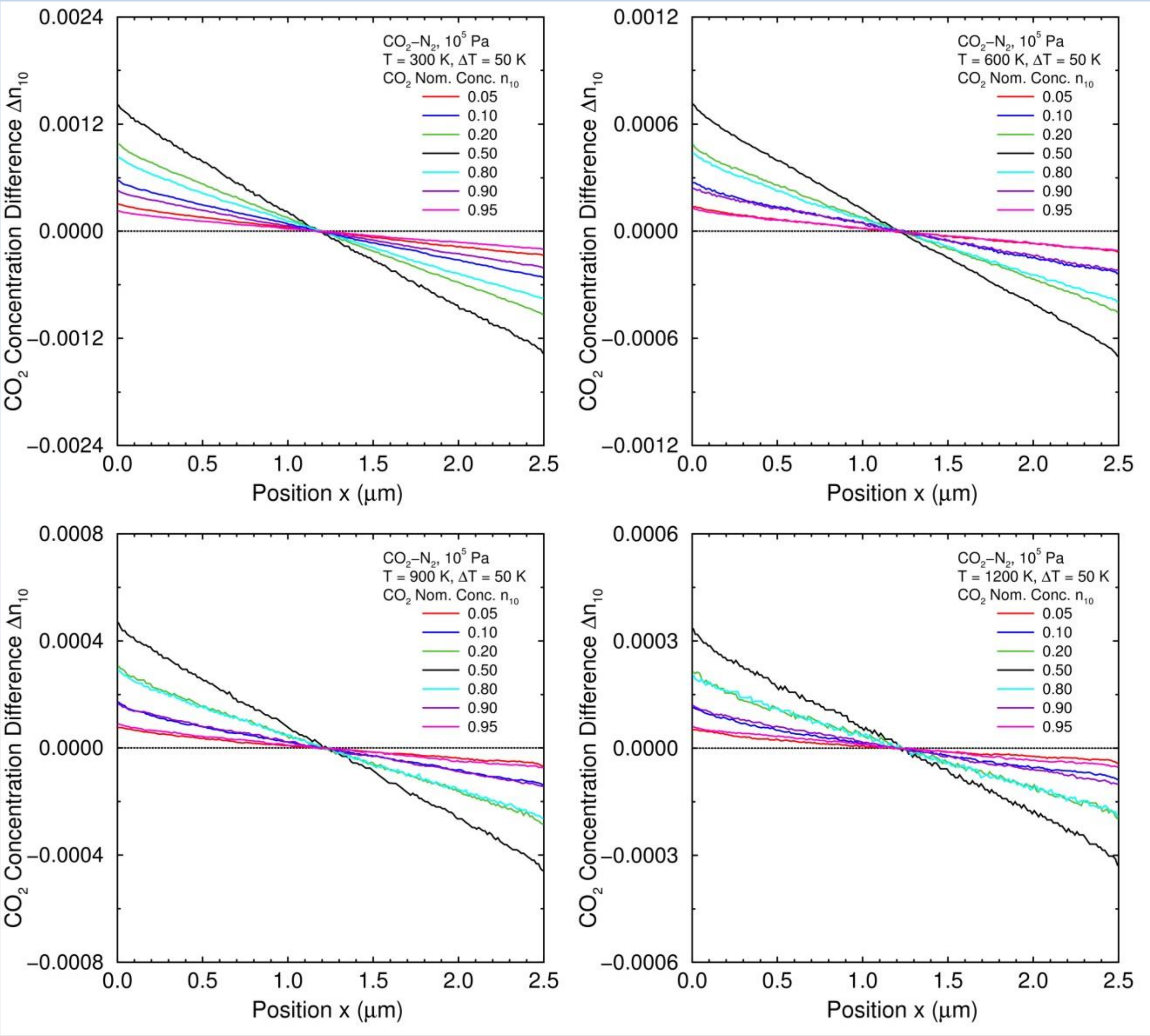


Thermal diffusion simulations

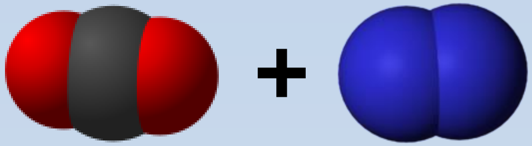
- CO_2-N_2 mixtures
- 7 nominal CO_2 concentrations
  - 5, 10, 20, 50, 80, 90, 95%
- 4 nominal gas temperatures
  - T = 300, 600, 900, 1200 K
- Fourier flow – motionless gas with different wall temperatures
  - Temp. difference: ΔT = 50 K
- Total of 28 combinations

All 28 concentration profiles at right

- Profiles scale roughly with $\Delta T/T$
- Profiles scale roughly with product of N_2 & CO_2 nominal concentrations
- Will need derivative dn_{10}/dx



CO_2-N_2 Thermal Diffusion Factor from DSMC Simulations



$$\alpha_{12} = \frac{-T\left(dn_{10}/dx\right)}{n_{10}\left(1-n_{10}\right)\left(dT/dx\right)}$$

Thermal diffusion factor α_{12} is found from temperature & concentration

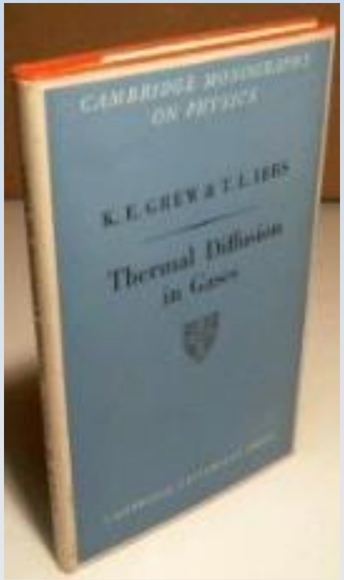
- Not VSS α (alas, same symbol)
- Use previously shown profiles
  - CO_2 concentration n_{10}
  - Temperature T
  - Position x
- Same 28 values shown two ways
  - Plot α_{12} vs. n_{10} for fixed T
  - Plot α_{12} vs. T for fixed n_{10}

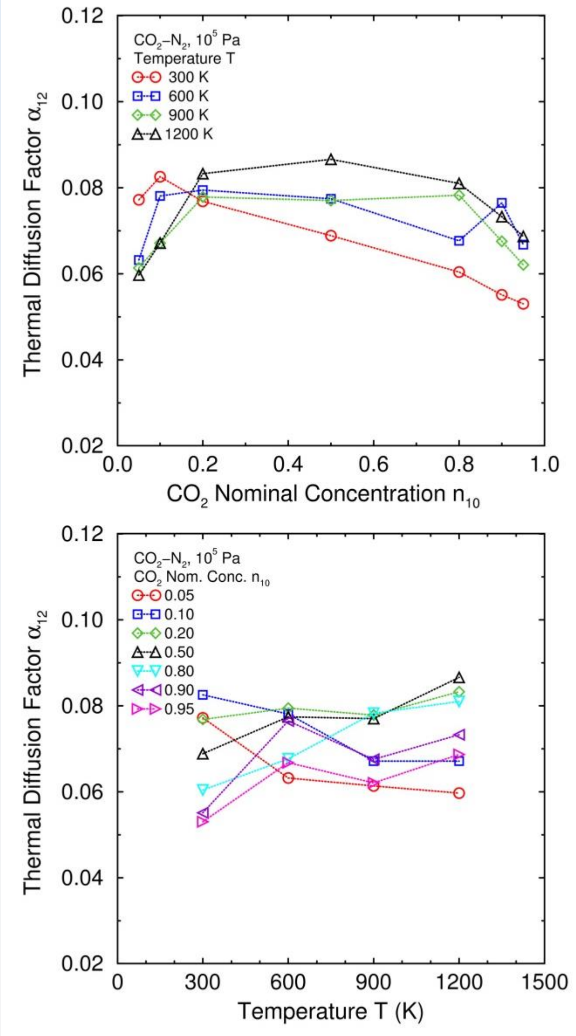
DSMC values have $\alpha_{12} = 0.071\pm0.009$

- Weak dependence on both temperature & concentration

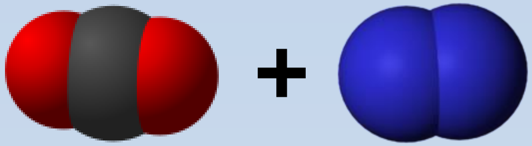
Grew & Ibbs have α_{12} = 0.036-0.061

- Around room temperature





Effect of Molecular Model



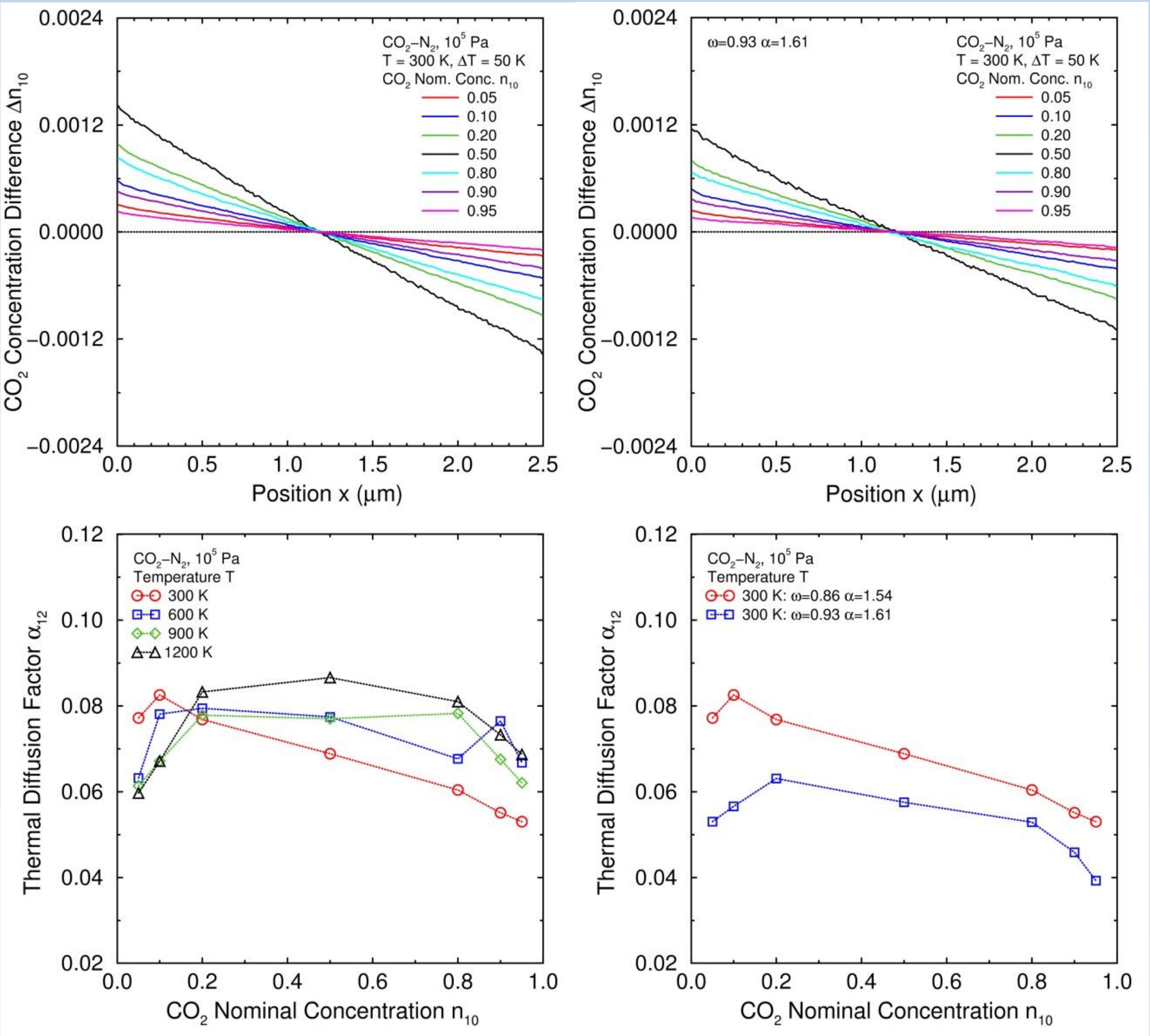
Thermal diffusion factor α_{12} is sensitive to molecular model

- **Present: VSS ω = 0.86, α = 1.54**
  - **Viscosity μ over T = 300-600 K**
  - **Clark Jones and Furry (1946)**
- **Bird: VSS ω = 0.93, α = 1.61**
  - **Viscosity μ at T = 300 K**
  - **Slope $d\mu/dT$ at T = 300 K**

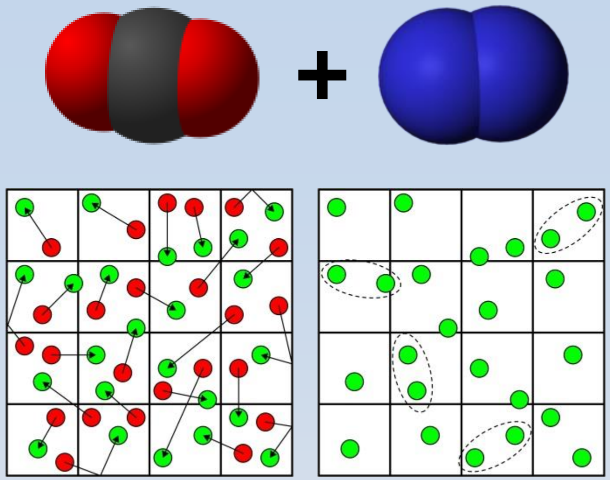
Thermal diffusion α_{12} values at 300 K

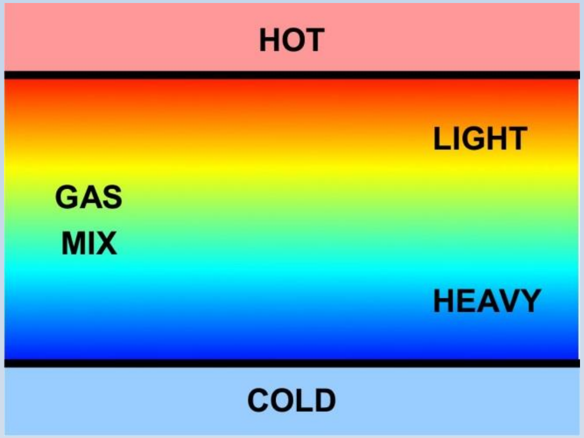
- **Do not confuse with α for VSS**
- **Present: α_{12} ~ 0.07**
- **Bird: α_{12} ~ 0.05**
- **Expt: α_{12} ~ 0.036-0.061**

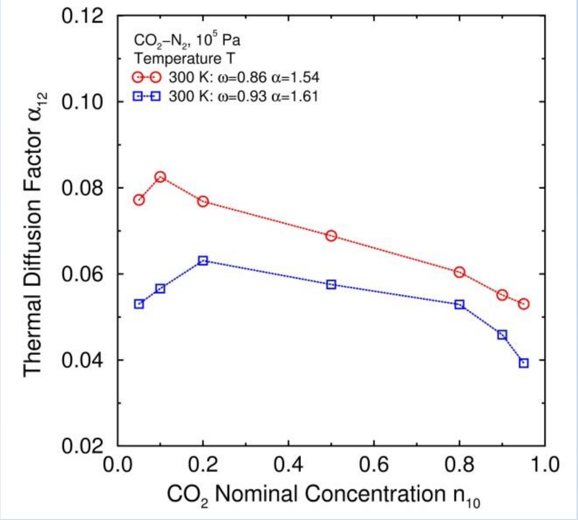
Apparently both viscosity and its temperature dependence must be matched for thermal diffusion



Conclusions







The Direct Simulation Monte Carlo (DSMC) method can be used to simulate thermal diffusion

- **Thermal diffusion is rather sensitive to the fine details of the molecular model employed**

The VSS molecular model for carbon dioxide is not accurate enough for quantitative predictions

- **If the VSS model is restricted to a small temperature range (e.g., room temperature), its results are in reasonable agreement with experimental results (which have significant uncertainty)**

To represent CO_2 over a wide temperature range, a more general model than VSS is needed

- **Such a model must be compatible with the general architecture of the DSMC algorithm**

In hindsight, the following hierarchy of complexity in molecular collision models is clear

- **Monatomics (Ar, He) are straightforward, simple diatomics (N_2, O_2) are tractable, but complicated polyatomics (CO_2, CH_4, H_2O) are difficult**