

The Boltzmann Equation and the Chapman-Enskog Solutions

John W Daily



How to Proceed

- To develop a more complete theory of transport we must be able to have an accurate picture of the spatial and time variation of the velocity distribution.
- The method for doing this involves solving an equation that describes the evolution of the velocity distribution function.



Boltzmann's Equation

- Boltzmann's equation describes the evolution of the velocity distribution function in phase space.
- Phase space is the the multi-dimensional space including physical space, velocity space and time.
- Generally $f(\vec{x}, \vec{c}, t)$
- If we know f , then all the transport properties can be calculated.



- Boltzmann's equation is of the form

$$\left(\frac{\partial f}{\partial t} + c_j \frac{\partial f}{\partial x_j} + \frac{\partial}{\partial x_j} [F_j f] \right) = \left(\frac{\partial f}{\partial t} \right)_{coll}$$

- The terms on the left describe the evolution of the distribution function in time, physical space and velocity space.
- The term on the right accounts for collisions that change the velocity of a particle.



Left Hand Side

- The first two terms should be familiar from the Navier-Stokes equations. They represent rate of change with time and convection.
- The third term represents convection in velocity space due to applied body forces, F . In other words, due to $F = ma$.



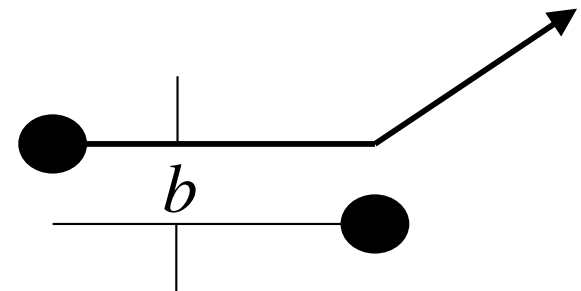
Collision Integral

- One may show (HCB) that

$$\left(\frac{\partial f}{\partial t} \right)_{coll} = \int \int \int (f'_k f'_j - f_k f_j) g_{kj} b db d\epsilon d\vec{c}$$

- Where

- b impact factor
- g_{kj} relative collision velocity
- ϵ angle of approach out of plane
- Prime indicates after collision



- Boltzmann's equation is therefore an integro-differential Equation, meaning it has both differential and integral terms.
- It was first solved independently by Chapman and Enskog using asymptotic methods.
- In the small departure from equilibrium limit the solution results in the Navier-Stokes equations and provides expressions for the transport properties.



The Transport Terms

- The Chapman-Enskog solution leads to the following transport terms

$$\mu_k = \frac{5}{16} \frac{\sqrt{\pi m_k k_B T}}{\pi \sigma_k^2 \Omega^{(2,2)*}} \quad \lambda_k = \frac{5}{2} c_{v,k} \mu_k$$

$$D_{kj} = \frac{3}{16} \frac{\sqrt{2 \pi k_B^3 T^3 / \mu_{jk}}}{P \pi \sigma_{jk}^2 \Omega^{(1,1)*}}$$



The Collision Integrals

- The only terms we have not seen are the collision integrals

$$\Omega^{(l,s)*}(T^*) = \frac{2}{(s-1)!T^{*(s+2)}} \int_0^\infty \exp\left[\frac{-g^{*2}}{T^*}\right] g^{*(2s+3)} Q^{(l)*}(g^*) dg^*$$

- where

$$Q^{(l)*}(g^*) = \frac{2}{1 - \frac{1}{2} \left[\frac{1 + (-1)^l}{l+1} \right]} \int_0^\infty (1 - \cos^l \chi) b^* db^*$$

- and

$$\chi(g^*, b^*) = \pi - 2b^* \int_0^\infty \frac{dr^* / r^*}{\sqrt{1 - (b^*)^2 / (r^*)^2 - \phi^*(r^*) / g^{*2}}}$$



The Collision Integrals

- To calculate the collision integrals requires knowing the intermolecular potential. This is typically Lennard-Jones:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Non-Dimensionalization of the Collision Integrals

- Typically one normalizes energy on ε and length on σ

$$T^* = kT / \varepsilon,$$

$$\phi^* = \phi / \varepsilon$$

$$r^* = r / \sigma$$

etc.

- The one can tabulate the integral values.



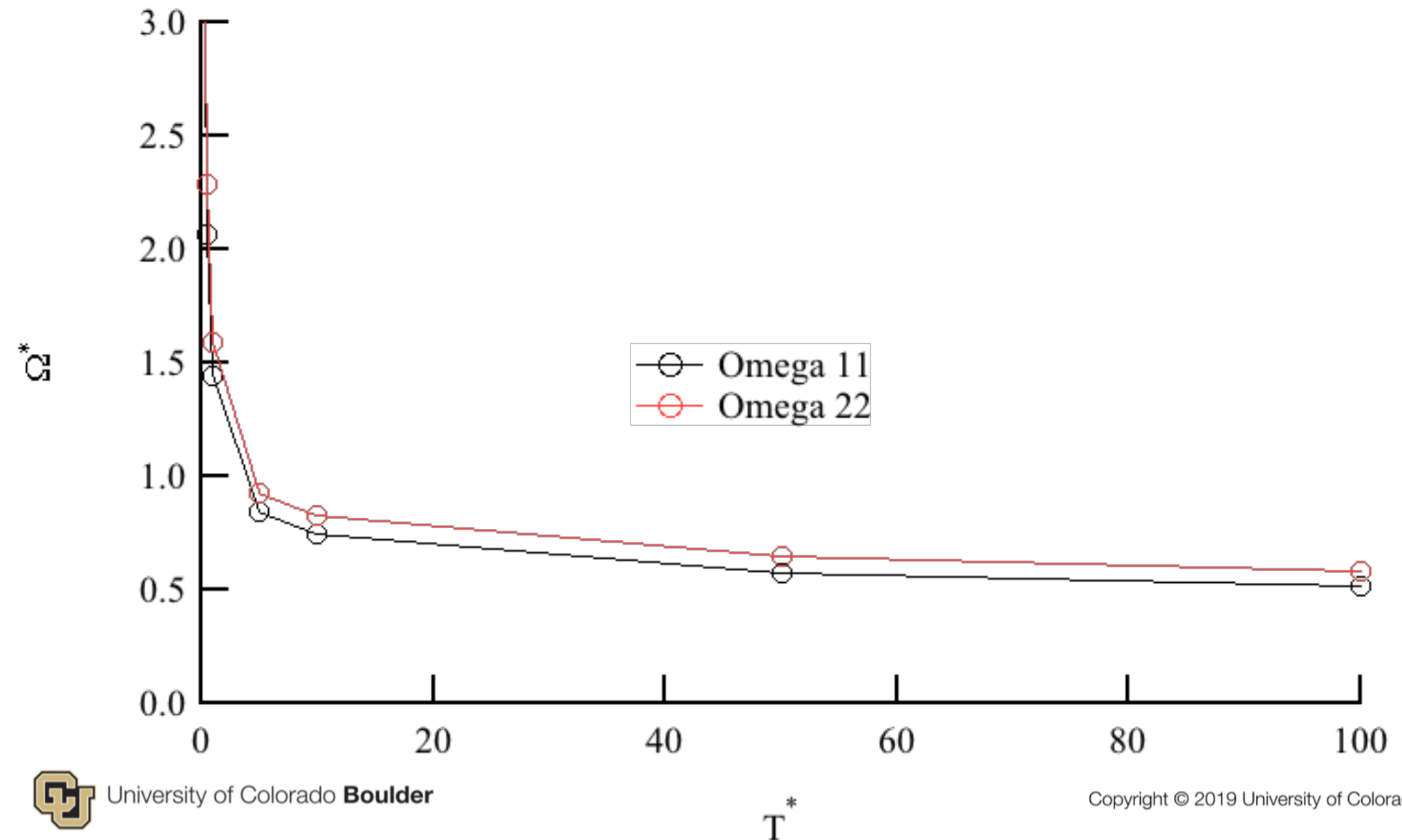
Values for $\Omega^{(l,s)*}(T^*)$ are tabulated below for the Lennard-Jones 6,12 potential.

T^*	$\Omega^{(2,2)*}$	$\Omega^{(1,1)*}$	T^*	$\Omega^{(2,2)*}$	$\Omega^{(1,1)*}$	T^*	$\Omega^{(2,2)*}$	$\Omega^{(1,1)*}$	T^*	$\Omega^{(2,2)*}$	$\Omega^{(1,1)*}$
0.3	2.785	2.662	1.3	1.399	1.273	2.6	1.081	0.9878	4.6	0.9422	0.8568
0.35	2.628	2.476	1.35	1.375	1.253	2.7	1.069	0.977	4.7	0.9382	0.853
0.4	2.492	2.318	1.4	1.353	1.233	2.8	1.058	0.9672	4.8	0.9343	0.8492
0.45	2.368	2.184	1.45	1.333	1.215	2.9	1.048	0.9576	4.9	0.9305	0.8456
0.5	2.257	2.066	1.5	1.314	1.198	3	1.039	0.949	5	0.9269	0.8422
0.55	2.156	1.966	1.55	1.296	1.182	3.1	1.03	0.9406	6	0.8963	0.8124
0.6	2.065	1.877	1.6	1.279	1.167	3.2	1.022	0.9328	7	0.8727	0.7896
0.65	1.982	1.798	1.65	1.264	1.153	3.3	1.014	0.9256	8	0.8538	0.7712
0.7	1.908	1.729	1.7	1.248	1.14	3.4	1.007	0.9186	9	0.8379	0.7556
0.75	1.841	1.667	1.75	1.234	1.128	3.5	0.999	0.912	10	0.8242	0.7424
0.8	1.78	1.612	1.8	1.221	1.116	3.6	0.9932	0.9058	20	0.7432	0.664
0.85	1.725	1.562	1.85	1.209	1.105	3.7	0.987	0.8998	30	0.7005	0.6232
0.9	1.675	1.517	1.9	1.197	1.094	3.8	0.9811	0.8942	40	0.6718	0.596
0.95	1.629	1.476	1.95	1.186	1.084	3.9	0.9755	0.8888	50	0.6504	0.5756
1	1.587	1.439	2	1.175	1.075	4	0.97	0.8836	60	0.6335	0.5596
1.05	1.549	1.406	2.1	1.156	1.057	4.1	0.9649	0.8788	70	0.6194	0.5464
1.1	1.514	1.375	2.2	1.138	1.041	4.2	0.96	0.874	80	0.6076	0.5352
1.15	1.482	1.346	2.3	1.122	1.026	4.3	0.9553	0.8694	90	0.5973	0.5256
1.2	1.452	1.32	2.4	1.107	1.012	4.4	0.9507	0.8652	100	0.5882	0.517
1.25	1.424	1.296	2.5	1.093	0.996	4.5	0.9464	0.861			

Table E.1: Lennard-Jones 6-12 Collision Integrals (from Hirschfelder, Curtis and Bird [10]. Also in Bird, Stewart and Lightfoot [11]).



Lennard-Jones 6-12



Lennard-Jones Parameters

Species	$\sigma / \text{\AA}$	$(\epsilon/k_B) / \text{K}$
He	2.55	10
Ne	2.82	32
Ar	3.47	114
Kr	3.66	178
Xe	4.05	230
H ₂	2.83	60
D ₂	2.73	69
CO	3.70	105
N ₂	3.74	82
NO	3.49	117
O ₂	3.48	103
CO ₂	3.94	201
N ₂ O	3.78	249
NO ₂	4.68	146
"	3.46	357
H ₂ O	2.71	506
NH ₃	2.90	558
CH ₄	3.79	153
C ₂ H ₂	4.13	224



Mixtures

- Mixtures add complexity to the theory. As a result, in calculating viscosity or thermal conductivity, various empirical mixture rules are used. For example:
- Wilke formula

$$\mu_{mix} = \sum_i \frac{x_i \mu_i}{\sum_j x_j \Phi_{ij}}$$

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2$$



Multicomponent Diffusion

- It turns out that when Fick's Law of diffusion isn't valid, then multicomponent diffusion depends on the concentrations of all the species in the mixture.
- Commonly called Maxwell-Stefan diffusion, calculating diffusion coefficients or fluxes requires simultaneous solution of the multicomponent Navier-Stokes equations.



Multicomponent Diffusion

$$\begin{aligned}\vec{\nabla} x_i = & \sum_{j=1}^N \left(\frac{x_i x_j}{D_{ij}} \right) (\vec{v}_j - \vec{v}_i) + (y_i - x_i) \frac{\vec{\nabla} p}{p} + \left(\frac{\rho}{p} \right) \sum_{j=1}^N y_i y_j (\vec{F}_i - \vec{F}_j) \\ & + \sum_{j=1}^N \left[\left(\frac{x_i x_j}{\rho D_{ij}} \right) \left(\frac{D_{Tj}}{y_j} - \frac{D_{Ti}}{y_i} \right) \right] \left(\frac{\vec{\nabla} T}{T} \right)\end{aligned}$$

Here x_i and y_i are the mole and mass fractions of species i respectively. The F_i are the species specific body forces per unit volume. The D_{ij} are the pairwise multicomponent diffusion coefficients and D_T the thermal diffusion coefficients.



Summary

- For pure substances viscosity and thermal conductivity can be measured or calculated once and for all.
- For mixtures, one can use either empirical mixture rules for viscosity and thermal conductivity, or more complex theory.
- For mass diffusion in mixtures, simple Fick's Law can be used for minor species, otherwise full multicomponent or some approximation must be used.

