

Transport Phenomena



<http://schoolworkhelper.net/2011/01/what-is-viscosity-application-flow-factors/>

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Transport properties in gases

9.1 *Viscosity – momentum transport*

9.2 *Thermal conductivity – energy transport*

9.3 *Diffusion – mass transport*

9.4 *Thermal diffusion equation*

9.5 *Solutions of the thermal diffusion equation*

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Viscosity



University of Queensland - Pitch drop experiment: Set up 1927, 9 drops so far.

Pitch has a viscosity ~ 230 billion (2.3×10^{11}) times that of water.

Pitch is a brittle solid – can be shattered with a hammer

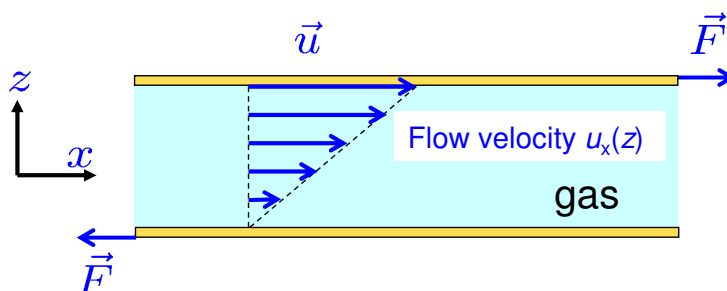


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9.1 Viscosity

- Viscosity is a measure for the resistance of a fluid to the deformation due to a shear stress τ_{ij} .

- Definition of viscosity η : $\tau_{xz} = \frac{F}{A} = \eta \frac{d\langle u_x \rangle}{dz}$



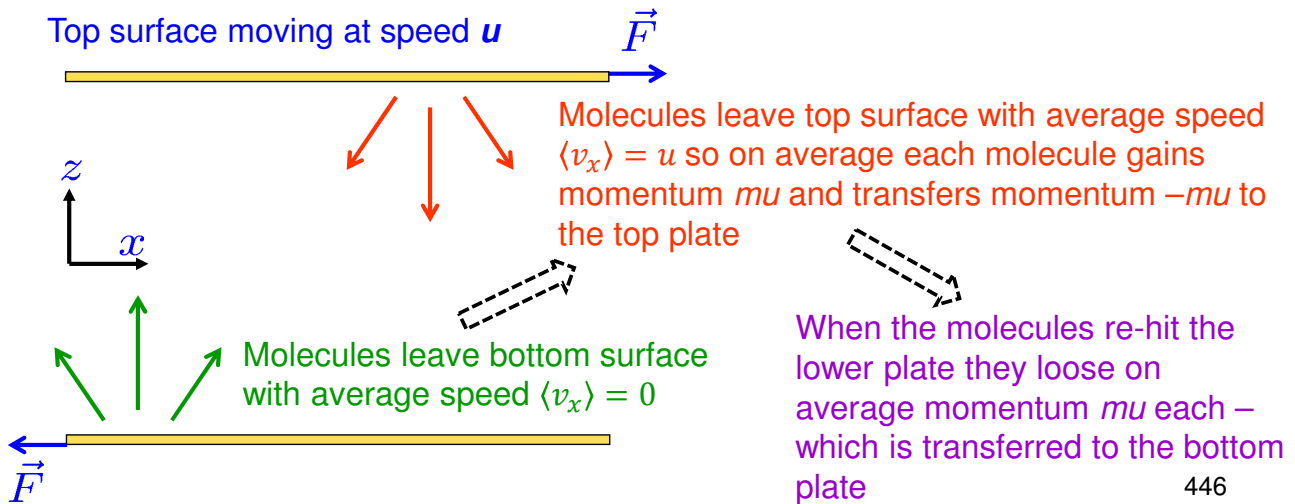
Top plate is transferring momentum F per second to the gas, across which it diffuses and arrives on bottom plate.

- **Boundary conditions:** the average velocity in x -direction, $\langle v_x \rangle$, must be zero at the lower plate and similar to that of the moving top plate of area A .

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Viscosity as momentum transfer

- We are deriving a viscosity coefficient for the situation where the gas can be treated as a continuous fluid, but to understand how momentum is being transferred, consider 'molecular flow' case where the mean free path is greater than the plate separation.
- Key idea: when gas molecules hit a surface they leave with a velocity distribution characteristic of surface – they are 'thermalised'



Viscosity

- Units of viscosity are $\text{Pa}\cdot\text{s} = \text{Nm}^{-2}\text{s}$.

$$\tau_{xz} = \frac{F}{A} = \eta \frac{d\langle u_x \rangle}{dz}$$

- The force is the rate of change of momentum.
- Therefore, τ_{xz} corresponds to the transverse momentum transported across each square meter per second, and τ_{xz} is equal to the flux of momentum.
- *Note:* we need to use a minus sign as the momentum flux goes from regions of high transverse velocities to those of lower velocities, which is opposite to the velocity gradient.

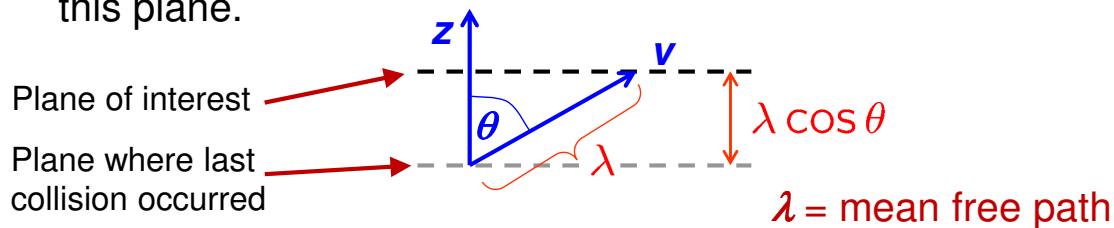
➡ **momentum flux** $\Pi_z = -\eta \frac{\partial \langle u_x \rangle}{\partial z}$

Viscosity of a gas

- Recall (chapter 8 – deriving pressure): the number of molecules hitting unit area per second is:

$$\begin{array}{c}
 \text{No of candidate} \\ \text{molecules/unit} \\ \text{area} \\
 \text{Fraction within} \\ \text{range } v \text{ to } v+dv \\
 \text{Fraction within} \\ \text{range } \theta \text{ to } \theta+d\theta \\
 v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta
 \end{array}$$

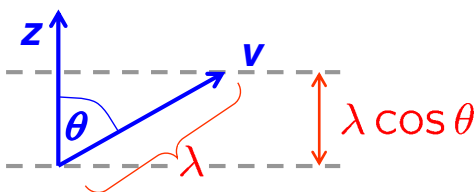
- Consider molecules travelling at an angle θ to the z -axis at a particular plane and work out net flow of momentum through this plane.



- Molecules crossing a plane of constant z will have travelled a distance λ , or a distance $\lambda \cos \theta$ parallel to the z -axis, since their last collision.

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Viscosity



- Over the travelled distance $\lambda \cos \theta$ the average velocity $\langle u_x \rangle$ will increase by

$$\left(\frac{\partial \langle u_x \rangle}{\partial z} \right) \lambda \cos \theta$$

- Therefore, these upwards-travelling molecules bring an excess momentum in the x -direction that is given by

$$- m \left(\frac{d \langle u_x \rangle}{dz} \right) \lambda \cos \theta$$

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Viscosity

- The net **x**-momentum brought to the plane per unit area is the net flux of **x**-momentum per unit area transported across it.

Fraction within range v to $v+dv$
 Fraction within range θ to $\theta+d\theta$
 Mean extra momentum per molecule

No of candidate molecules/unit area

$$\begin{aligned}
 \Pi_z &= \int_0^\infty \int_0^\pi v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta m \left(-\frac{\partial \langle u_x \rangle}{\partial z} \right) \lambda \cos \theta \\
 &= \frac{1}{2} n m \lambda \underbrace{\int_0^\infty v f(v) dv}_{\langle v \rangle} \left(-\frac{\partial \langle u_x \rangle}{\partial z} \right) \underbrace{\int_0^\pi \cos^2 \theta \sin \theta d\theta}_{2/3} \\
 &\Rightarrow \Pi_z = \underbrace{-\frac{1}{3} n m \lambda \langle v \rangle}_{\text{viscosity}} \left(\frac{\partial \langle u_x \rangle}{\partial z} \right)
 \end{aligned}$$

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Viscosity

$$\eta = \frac{1}{3} n m \lambda \langle v \rangle$$

dynamic viscosity

- The expression for the viscosity has important consequences:

- η is independent of **pressure**.

Because $\lambda \approx 1/(\sqrt{2}n\sigma) \propto n^{-1}$

the viscosity is independent of the number density **n** at constant temperature and thus independent of pressure.

(σ is the collision cross section)

Note:

Kinematic viscosity is defined as

$$\nu = \eta / \rho$$

It describes the diffusivity of momentum.

Viscosity

$$\eta = \frac{1}{3}nm\lambda \langle v \rangle$$

dynamic viscosity

- Substitute $\lambda = (\sqrt{2}n\sigma)^{-1}$, and $\langle v \rangle = (8k_B T / \pi m)^{1/2}$

$$\eta = \frac{2}{3\sigma} \left(\frac{mk_B T}{\pi} \right)^{1/2}$$

- **T** dependence: $\eta \propto T^{1/2}$

In contrast, the viscosity of liquids decreases with increasing **T**.

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Viscosity

$$\eta = \frac{2}{3\sigma} \left(\frac{mk_B T}{\pi} \right)^{1/2} \quad \text{viscosity}$$

- Further $\eta \propto \frac{\sqrt{m}}{\sigma}$

Careful:

We made **many** approximations in order to get the expressions for η . In particular we assumed that:

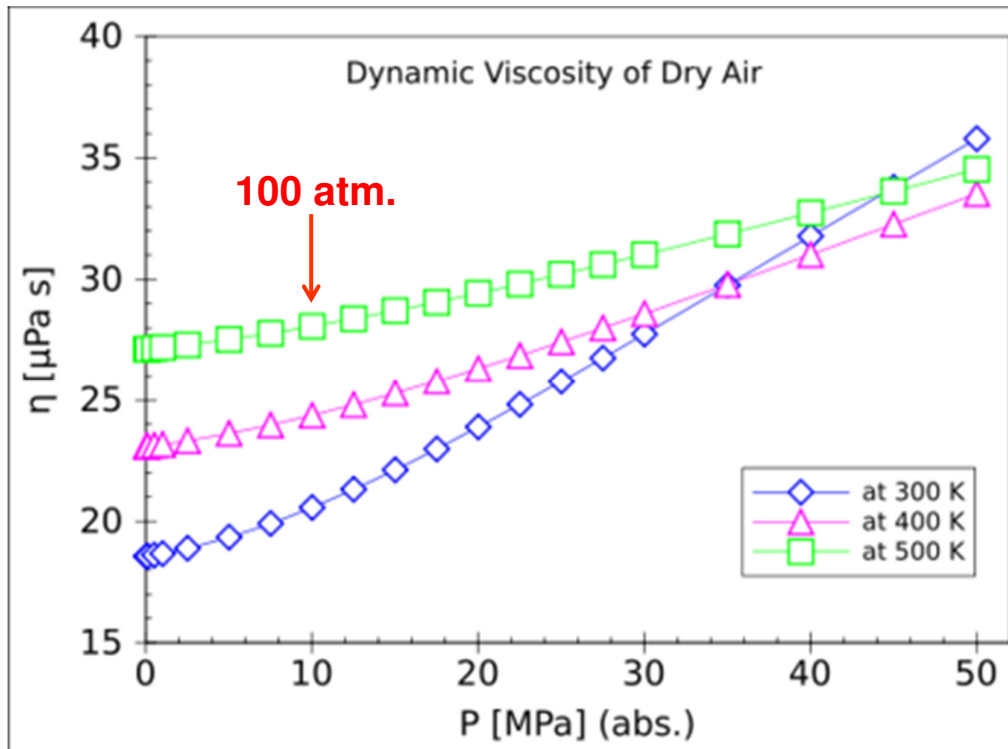
$$L \gg \lambda \gg d \quad \left(\begin{array}{l} L = \text{container size,} \\ d = \text{molecule diameter} \end{array} \right)$$

Scale of flow must be much greater than mean free path

Requires not too high pressure
(avoiding many particle collisions, and effect of long range attraction that can give an extra coupling of the molecules motion)

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Viscosity



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http://wapedia.mobi/en/File:Air_dry_dynamic_visosity_on_pressure_temperature.svg

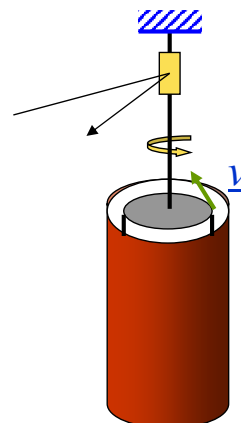
Viscosity

$$\eta = \frac{1}{3}nm\lambda \langle v \rangle$$

viscosity

- Finally, the prefactor **1/3** is also not completely correct, because we used a uniform velocity distribution, although in the presence of a **v** – gradient this has to be modified.

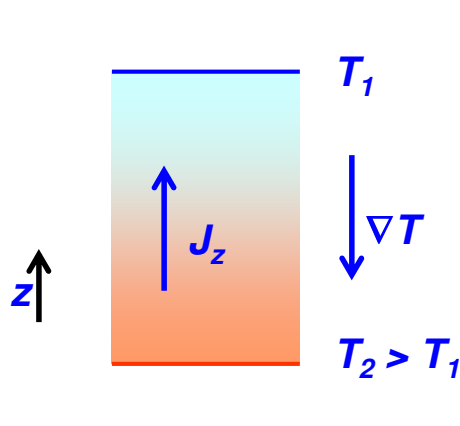
- Note: the viscosity can be measured from the damping of torsional oscillations of a cup in a cylinder (Couette-geometry).
- The method was developed by Maxwell.



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9.2 Thermal Conductivity

- We introduced heat as a form of energy.
- Heat quantifies the transfer of Energy in response to a temperature gradient.
- The amount of heat that flows along a temperature gradient will depend on the *thermal conductivity* of the material used.



- By definition, flows from hot to cold.
- Define \mathbf{J} as the *heat flux* (here J_z along in one dimension).

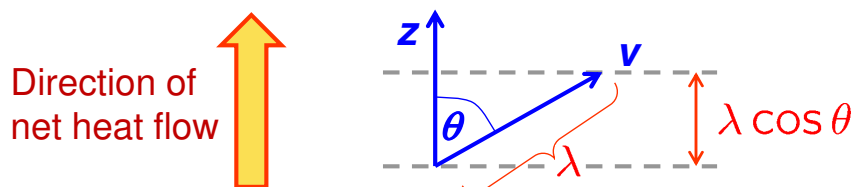
$$J_z = -\kappa \left(\frac{\partial T}{\partial z} \right)$$

Units: $\text{Js}^{-1}\text{m}^{-2} = \text{W m}^{-2}$

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Thermal Conductivity

- κ is the *thermal conductivity* - it is **material specific**.
 - The general expression (3D) of heat flux is:
- $$\vec{J} = -\kappa \nabla T$$
- In a similar way to the derivation of the expression for viscosity, we will consider the 'excess heat' being brought to a plane of constant z drawn perpendicular to the temperature gradient:

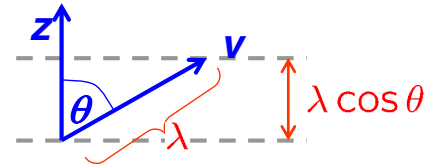


- Molecules crossing the plane will have travelled a distance λ , i.e. a distance $\lambda \cos \theta$ parallel to the z -axis, since their last collision. It is assumed that at each collision the molecules are 'thermalised' – i.e. pick up a velocity distribution characteristic of the local temperature of the gas at the position of the last collision

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Thermal conductivity

- The excess heat energy brought by a molecule to the plane perpendicular to z is then given by:



$$C_{\text{molecule}} \times \Delta T = C_{\text{molecule}} \left(\frac{\partial T}{\partial z} \right) \lambda \cos \theta$$

- The total thermal energy transported across unit area in unit time is given by the heat flux

$$\begin{aligned} J_z &= \int_0^\infty dv \int_0^\pi \left(-C_{\text{molecule}} \frac{\partial T}{\partial z} \lambda \cos \theta \right) v \cos \theta n f(v) \frac{1}{2} \sin \theta d\theta \\ &= -\frac{1}{2} n C_{\text{molecule}} \lambda \int_0^\infty v f(v) dv \left(\frac{\partial T}{\partial z} \right) \int_0^\pi \cos^2 \theta \sin \theta d\theta \\ &= -\frac{1}{3} n C_{\text{molecule}} \lambda \langle v \rangle \left(\frac{\partial T}{\partial z} \right) \end{aligned}$$

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Thermal conductivity

- Thus the thermal conductivity is given by

$$\kappa = \frac{1}{3} C_V \lambda \langle v \rangle$$

where $C_V = n C_{\text{molecule}}$ is the heat capacity per unit volume.

- What do we learn from this expression?

- Like the viscosity, κ is independent of pressure for the same reason:

$$\lambda \approx 1/(\sqrt{2}n\sigma) \propto n^{-1} \quad \text{and} \quad C_V \propto n$$

- Same T dependence: $\kappa \propto T^{1/2}$

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Thermal conductivity

- Substituting $\lambda = (\sqrt{2}n\sigma)^{-1}$ and $\langle v \rangle = (8k_B T / \pi m)^{1/2}$

$$\kappa = \frac{2}{3\sigma} C_{\text{molecule}} \left(\frac{k_B T}{\pi m} \right)^{1/2}$$

- Further we have $\kappa \propto 1/(\sigma\sqrt{m})$ at constant temperature.

- The similarity between η and κ suggests that

$$\frac{\kappa}{\eta} = \frac{C_{\text{molecule}}}{m} \quad \longrightarrow \quad \boxed{\kappa = C_{v,s} \eta}$$

specific heat capacity $C_{v,s}$

- Remember, however, derivations of η and κ are based on several assumptions and thus hold only in a limited way.

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Thermal conductivity: more refined formulae

- We made many assumptions to derive $\kappa = C_{v,s} \eta$
- The expression is quite good, but it does not take account of the fact that **a faster moving molecule carries more heat in its translational degree of freedom than a slower moving one**. If this effect is taken into account for a monatomic gas, where all the heat is stored in the translational degrees of freedom, then the thermal conductivity is increased by a factor of $5/2$ and becomes:

$$\kappa = \frac{5}{2} C_{v,s} \eta$$

- Most gases are molecules and also have heat stored in **translational**, **rotational** and **vibrational** degrees of freedom. Whilst in every collision the energy can be redistributed in these different degrees of freedom, the actual values of these energies for a particular molecule are not directly correlated to the translational energy. It makes sense, therefore, to split the specific heat capacity as $C_{v,s} = C'_{v,s} + C''_{v,s}$, with the first term containing translational and the second term the remaining degrees of freedom, and apply the correction only to the translational part, giving:

$$\kappa = \left(\frac{5}{2} C'_{v,s} + C''_{v,s} \right) \eta$$

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Thermal conductivity: more refined formulae

$$\kappa = \left(\frac{5}{2} C'_{v,s} + C''_{v,s} \right) \eta$$

- $C'_{v,s}$ and $C''_{v,s}$ can be written in terms of the full value for specific heat capacity $C_{v,s}$, and γ giving **Eucken's formula**:

$$\kappa = \frac{1}{4} (9\gamma - 5) \eta C_{v,s}$$

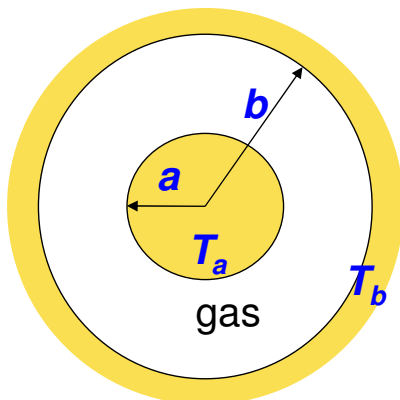
(For a monatomic gas with $\gamma=5/3$, and there are no non-translational degrees of freedom in which heat can be stored the, so $C''_v = 0$ and the thermal conductivity Eucken's formula gives $\kappa = \frac{5}{2} C_{v,s} \eta$ as previously)

- More accurate calculations can be done (**Chapman-Enskog**) but these are beyond the scope of this course.

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Measuring thermal conductivity

Coaxial cylinder method:



- Gas of interest is filled between 2 coaxial cylinders
- The temperature of the outer cylinder is fixed to T_b by a T -bath.
- The inner cylinder is heated at a rate Q per unit length (Wm^{-1}) until it reaches T_a . (Q is the power supplied and thus known).

It is: $Q = 2\pi r J_r = r 2\pi (-\kappa \partial T / \partial r)$

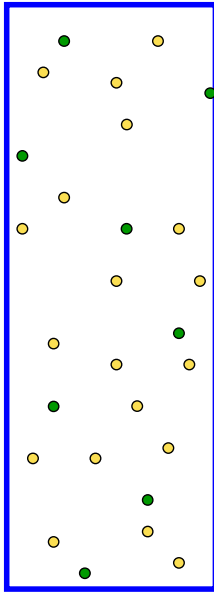
Integration then yield: $Q \int_a^b \frac{dr}{r} = -2\pi\kappa \int_{T_a}^{T_b} dT$



$$\kappa = \frac{Q \ln b/a}{2\pi T_a - T_b}$$

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9.3 Diffusion



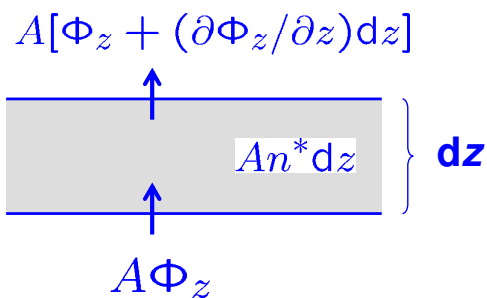
- Consider a distribution of similar molecules of which $n^*(z)$ per unit volume are labelled.
- The flux Φ_z of labelled molecules in z-direction is measured in $\text{m}^{-2}\text{s}^{-1}$

$$\Phi_z = -D \left(\frac{\partial n^*}{\partial z} \right)$$

↑
self-diffusion coefficient

- In 3D this equation is written as $\underline{\Phi} = -D \underline{\nabla} n^*$
... and known as **Fick's law**.⁴⁶⁴

Diffusion



- Now consider a thin layer of gas of thickness dz and area A .

- The flux into the slab is $A\Phi_z$.

- And the flux out is $A[\Phi_z + (\partial\Phi_z/\partial z)dz]$
- The difference in the two fluxes must be balanced by the time-dependent changes in the number of labelled particles inside the layer

$$\frac{\partial}{\partial t}(n^* A dz) = -A \frac{\partial \Phi_z}{\partial z} dz$$

Diffusion Coefficient

- Derivation of D , using kinetic theory:

The excess labelled molecules hitting unit area per second is

$$\begin{aligned}\Phi_z &= \int_0^\pi \int_0^\infty d\theta dv v \cos \theta f(v) \frac{1}{2} \sin \theta \left(-\frac{\partial n^*}{\partial z} \lambda \cos \theta \right) \\ &= \frac{1}{3} \lambda \langle v \rangle \frac{\partial n^*}{\partial z}\end{aligned}$$

- Hence

$$D = \frac{1}{3} \lambda \langle v \rangle = \frac{2}{3n\sigma} \left(\frac{k_B T}{\pi m} \right)^{1/2}$$

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Diffusion Coefficient

Implications:

- $D \propto p^{-1}$: because $\lambda \propto n^{-1}$ and therefore $D \propto n^{-1}$, at fixed temperature.
This holds well experimentally.
- $D \propto T^{3/2}$: because $p = nk_B T$ and $\langle v \rangle \propto T^{1/2}$ at fixed pressure.

- $D\rho = Dnm = \eta$

- Substituting $\langle v \rangle$ and λ gives: $D = \frac{1}{3} \lambda \langle v \rangle = \frac{2}{3n\sigma} \left(\frac{k_B T}{\pi m} \right)^{1/2}$

- $D \propto 1/(\sigma\sqrt{m})$ this is the same dependence as obtained for the thermal conductivity.

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Diffusion Coefficient

$$D = \frac{2}{3\pi n d^2} \left(\frac{k_B T}{\pi m} \right)^{1/2}$$

- To measure the self-diffusion coefficient, it is also possible to consider a mixture of two types of molecules with mass m_1 and m_2 and diameter d_1 and d_2 (**with assumption that the species we are interested in is in the minority**).
- For this we only need to replace the expression $\sigma = \pi d^2$ by $\sigma = \pi[(d_1 + d_2)/2]^2$ and m by the reduced mass $2m_1 m_2 / (m_1 + m_2)$:

$$D_{12} = \frac{2}{3\pi n (\frac{1}{2}[d_1 + d_2])^2} \left(\frac{k_B T (m_1 + m_2)}{2\pi m_1 m_2} \right)^{1/2}$$

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Summary

- Viscosity defined by $\Pi_z = -\eta \partial \langle u_x \rangle / \partial z$ is approximated by

$$\eta = \frac{1}{3} n m \lambda \langle v \rangle$$

Viscosity describes transverse momentum diffusion!

- Thermal conductivity defined by $J_z = -\kappa \partial T / \partial z$ is approximated by

$$\kappa = \frac{1}{3} C_V \lambda \langle v \rangle$$

C_V in this equation is heat capacity per unit volume, $= n \cdot C_{V,m}$

- Diffusion defined by $\Phi_z = -D \partial n^* / \partial z$ is approximated by

$$D = \frac{1}{3} \lambda \langle v \rangle$$

These relationships assume that $L \gg \lambda \gg d$.

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Summary

- Predicted dependences:

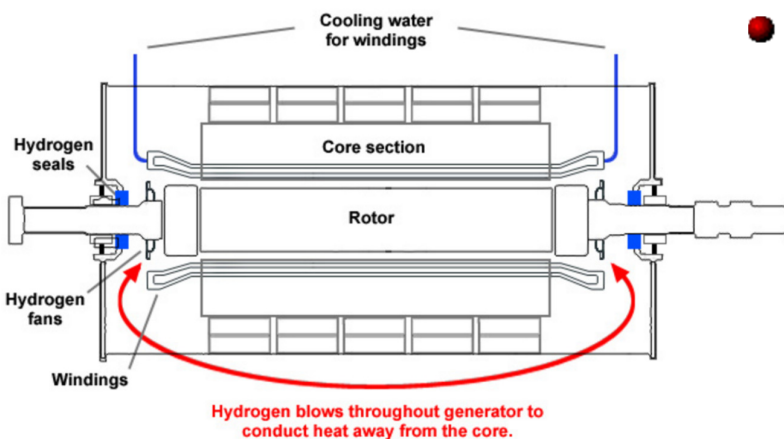
η	κ	D
$\propto p^0$	$\propto p^0$	$\propto p^{-1}$
$\propto T^{1/2}$	$\propto T^{1/2}$	$\propto T^{3/2}$
$\propto m^{1/2}d^{-2}$	$\propto m^{-1/2}d^{-2}$	$\propto m^{-1/2}d^{-2}$

- Typical values:

	Air	H ₂	He	Xe
Atomic/molar mass	29	2	4	131.3
Molar Heat Capacity at const. vol. C_v , mol/J/mol	2.50R	2.47R	1.50R	1.50R
Mean Free Path, λ /nm	68	111	173	38
Thermal Conductivity, κ mW/m/K	26.2	186.9	156.7	5.1
Viscosity, η /muPa.s	13.3	8.4	18.7	21

Examples of use of transport property scaling formulae

- Large (i.e. up to 1000MW) electricity generators (total UK average demand is 30GW) have a water cooled 'stator' in which the power is generated, and a rotating electromagnet that is gas cooled.



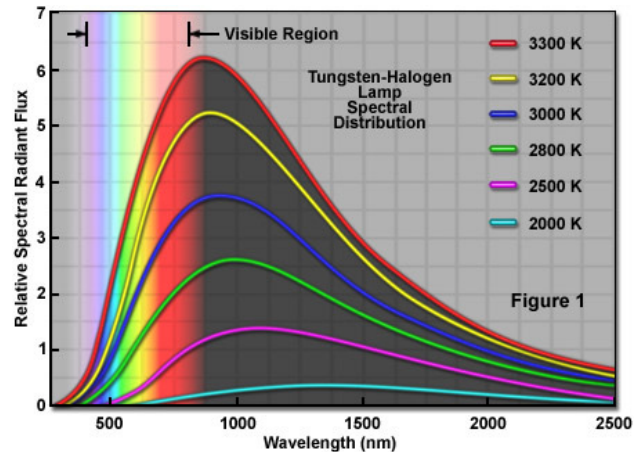
- Hydrogen's light mass and higher heat capacity (cf a noble gas) give it an excellent thermal conductivity, and it also has a low viscosity – both of which are independent of pressure – so one can increase the pressure (to 6bar) to increase the thermal capacity (ie its ability to carry heat away) of the gas.

<http://www.nova-gas.com/analyzers/hydrogen-purity>

- The hydrogen needs to be quite pure – a purity drop from 97 to 95% in a large generator can increase windage losses by 32%; - 685 kW for a 907 MW generator.

Examples of use: 'halogen' light bulbs

- Old style 'incandescent' bulbs rely on a hot tungsten filament. The hotter the filament, the more of its radiated power lies in the visible range:
- Tungsten evaporation from the filament controls the lifetime – typically a temperature of 2400K achieved.
- In a tungsten halogen bulb, a halogen is added to 'recycle' evaporated tungsten, but they are filled with high pressure (6-7bar) Xe gas – the high density of huge atoms reduces the diffusion rate of Tungsten and temperatures of 2700-2800K are standardly achieved, whilst retaining a good lifetime. The low heat capacity, slow atomic velocities and short mean free path of Xe give a low thermal conductivity, reducing conductive heat losses from the bulb.



9.4 Thermal/particle Diffusion Equation

- Recall: the heat flux \underline{J} is defined by

$$\underline{J} = -\kappa \underline{\nabla} T$$

- Mathematically this is similar to the equation of particle flux

$$\underline{\Phi} = -D \underline{\nabla} n^* \quad \text{in 3D.}$$

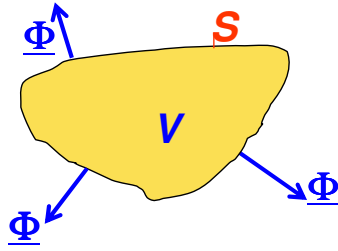
- In addition electric current is given by the current density \underline{J}_e :

$$\underline{J}_e = \sigma \underline{E} = -\sigma \underline{\nabla} \phi$$

(σ = conductivity, \underline{E} = electric field, ϕ = electric potential)

- c.f. Feynman's comment - "*the same equations have the same solutions*". - if there is a particle diffusion equation there must be also a thermal diffusion equation.

3D Diffusion Equation



- In 3D the total number of labelled particles that flow out of a closed surface **S** is given by

$$\int_S \underline{\Phi} \cdot d\underline{S}$$

- It is balanced by the rate of decrease of labelled particles inside the volume **V** surrounded by **S**:

$$\int_S \underline{\Phi} \cdot d\underline{S} = \frac{\partial}{\partial t} \int_V n^* dV$$

- Using Gauss' theorem $\int_S \underline{\Phi} \cdot d\underline{S} = - \int_V \underline{\nabla} \cdot \underline{\Phi} dV$

and substituting in $\underline{\Phi} = -D \underline{\nabla} n^*$ and equating integrands we obtain:

$$\frac{\partial n^*}{\partial t} = D \nabla^2 n^*$$

3D Diffusion equation

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Thermal Diffusion Equation

- Consider volume **V**: the total heat flow out of **V** through a closed surface **S** is given by

$$\int_S \underline{J} \cdot d\underline{S}$$

- This must be equal to the rate of loss of heat by the body so:

$$\int_S \underline{J} \cdot d\underline{S} = - \int_V c \frac{\partial T}{\partial t} dV$$

where **c** is the heat capacity per unit volume ($\text{JK}^{-1}\text{m}^{-3}$).

Gauss' theorem $\int_S \underline{J} \cdot d\underline{S} = \int_V \underline{\nabla} \cdot \underline{J} dV$ gives $\int_S \underline{\nabla} \cdot \underline{J} dV = - \int_V c \frac{\partial T}{\partial t} dV$

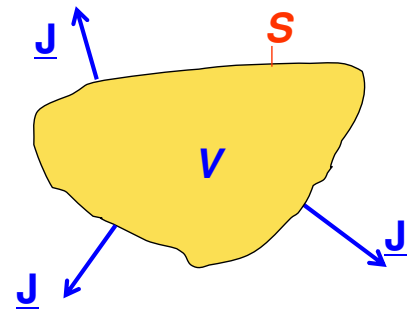
hence $\underline{\nabla} \cdot \underline{J} = -c \frac{\partial T}{\partial t}$ and substituting for **J** yields the thermal

diffusion equation

$$\frac{\partial T}{\partial t} = D \nabla^2 T$$

$$D = \kappa / c$$

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9.5 Solutions of the thermal diffusion equation

- We will now consider 3 'special cases' of the use of the diffusion equation – the first is the relaxation of a temperature profile – how long does it take the heat to flow to establish an equilibrium temperature distribution.
- Try looking for separable solutions *i.e.* ones of the form:

$$T(\mathbf{r}, t) = P(\mathbf{r})\tau(t)$$

The thermal diffusion equation becomes:

$$\frac{\partial T(\mathbf{r}, t)}{\partial t} = D\nabla^2 T(\mathbf{r}, t) \implies P(\mathbf{r}) \frac{d\tau(t)}{dt} = D\tau(t)\nabla^2 P(\mathbf{r})$$

writing
$$\frac{\tau'(t)}{\tau(t)} = \frac{D\nabla^2 P(\mathbf{r})}{P(\mathbf{r})} = -\alpha$$

we have for the time dependence of a particular solution:

$$\ln \tau(t) = -\alpha t + \text{const} \quad \text{and} \quad \tau(t) \propto e^{-\alpha t}$$

e.g. for real positive α , the solution decays exponentially with characteristic time $1/\alpha$.

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Relaxation of a temperature profile

- Now looking for the solution for the spatial part of $T(\mathbf{r}, t) = P(\mathbf{r})\tau(t)$

$$\nabla^2 P(\mathbf{r}) = -\frac{\alpha}{D} P(\mathbf{r})$$

- Try looking for plane wave solutions of the form: $P_k(\mathbf{r}) = P_{0,k} e^{i\mathbf{k}\cdot\mathbf{r}}$

$$\nabla^2 P_k(\mathbf{r}) = -k^2 P_k(\mathbf{r})$$

i.e. the solution works provided: $\alpha = k^2 D$

Short wavelength contributions decay much faster

- The general solution (for plane waves and hence real k) therefore has the form:

$$T(\mathbf{r}, t) = \sum_k P_{0,k} e^{i\mathbf{k}\cdot\mathbf{r}} \cdot e^{-k^2 D t}$$

- For real negative α , k becomes pure complex and we have exponential temperature profiles with distance – to make this happen in real life then at the 'large value of exponential' boundary you have to supply heat in at an ever increasing rate to match the generally increasing temperature with time – whilst not unphysical, it is in practical terms rather unusual.

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Relaxation of a temperature profile

- The general solution for k real: $T(\mathbf{r}, t) = \sum_k P_{0,k} e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-k^2 D t}$

To use this consider whether you have a temperature disturbance on a large length/volume/area in which case use Fourier transforms instead of sum, giving the general solution:

$$T(\mathbf{r}, t) = \int P_0(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-k^2 D t} d\mathbf{k}$$

Where $P_0(\mathbf{k})$ is the (n -dimensional) Fourier transform of the initial profile:

$$T(\mathbf{r}, 0) = \int P_0(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k} \quad \text{where: } P_0(\mathbf{k}) = \frac{1}{(2\pi)^n} \int T(\mathbf{r}, 0) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r}$$

- i.e., you decompose the original profile into Fourier components – each of which decays at a separate rate – so you let them decay for a time t , then add them up again to give the full solution a time t .
- **The solution at long times is dominated by the longest wavelength Fourier components as they have the longest time constants, τ :**

$$\begin{aligned} e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-\alpha t} &= e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-t/\tau} \\ &= e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-k^2 D t} \end{aligned} \quad \Rightarrow \quad \tau = \frac{1}{k^2 D} = \frac{\lambda^2}{4\pi^2 D}$$

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Relaxation of a temperature profile: finite object

- To treat a finite object you have to use a Fourier series instead of a Fourier transform, and consider the boundary conditions.
- Semi analytically (as opposed to completely numerically) this is possible for tessellating shapes for which either:

The boundary is a free one (no connection to take heat away – in which case just mirror the initial profile at that point (ensures zero temperature gradient and zero heat flow

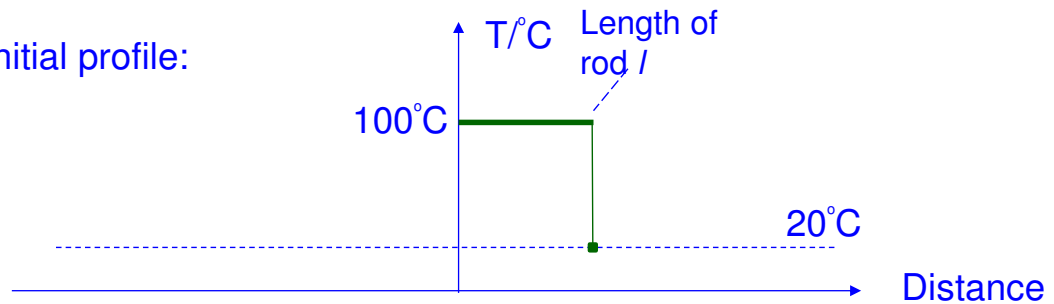
Or the boundary is a fixed temperature one – in which case mirror around the boundary with an initial temperature profile set up at the boundary so that the average across the initial jump at the boundary is as required:

E.g., a rod at 100°C is touched onto a surface maintained at 20°C

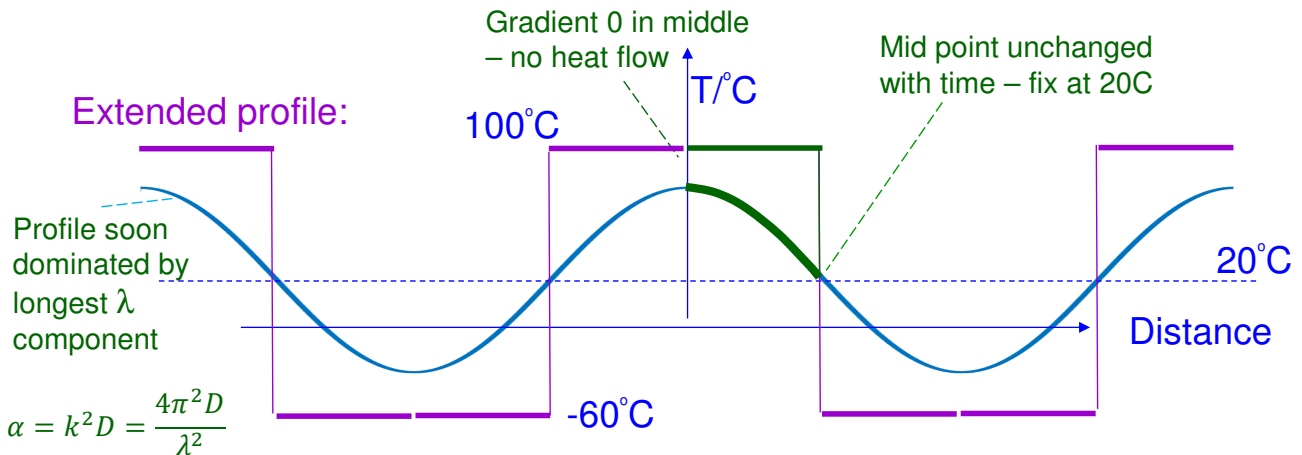
Relaxation of a temperature profile: finite object

Eg, a rod at 100°C is touched onto a surface maintained at 20°C

Desired initial profile:



Extended profile:



1D thermal diff. equ.: oscillating boundary cond.

- The 1D thermal diffusion equation is

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2}$$

- Recall general solution is of form:

$$T(\mathbf{r}, t) = \sum_k P_{0,k} e^{i\mathbf{k} \cdot \mathbf{r}} \cdot e^{-k^2 D t}$$

- Looking now in 1D for solutions which are periodic in time (for example a temperature profile in response to daily/yearly temperature fluctuations) we would wish to set

$$-i\omega = -Dk^2 \quad \longrightarrow \quad k^2 = \frac{i\omega}{D}$$

- Therefore $k = \pm(1+i)\sqrt{\frac{\omega}{2D}}$

- The spatial part of the wave that has the form e^{ikx} , will diverge for

$$\begin{aligned} \exp\left((i-1)\sqrt{\frac{\omega}{2D}}x\right) & \quad \text{when } x \rightarrow -\infty \\ \exp\left((-i+1)\sqrt{\frac{\omega}{2D}}x\right) & \quad \text{when } x \rightarrow \infty \end{aligned}$$

1D thermal diff. equ.: oscillating boundary cond.

- Let us solve a problem with a boundary condition at $x = 0$ for $x > 0$.
- We want to avoid divergences for $x \rightarrow \infty$, so use:

$$\exp\left((i-1)\sqrt{\frac{\omega}{2D}}x\right)$$

- A general solution for $x \geq 0$ can be of the form

$$T(x, t) = \sum_{\omega} A(\omega) e^{-i\omega t} e^{((i-1)\sqrt{\frac{\omega}{2D}}x)}$$

where we take the sum over all possible frequencies.

- To find, which frequencies are needed, we need to specify the boundary conditions for which we want to solve the differential equation.

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1D thermal diff. equ.: oscillating boundary cond.

- *Example:* Let us solve the thermal diffusion equation for the propagation of sinusoidal temperature waves into the ground (e.g. due to the **day-night** temperature cycle with a one day period or due to a **summer-winter** cycles with a period of 1 year)
- The boundary conditions can be written as

$$T(0, t) = T_0 + \Delta T \cos \Omega t$$

- Which can be rewritten as

$$T(0, t) = T_0 + \frac{\Delta T}{2} e^{i\Omega t} + \frac{\Delta T}{2} e^{-i\Omega t}$$

- However, at $x = 0$ the general solution is

$$T(0, t) = \sum_{\omega} A(\omega) e^{-i\omega t}$$

Comparison gives:

$$A(0) = T_0$$

$$A(-\Omega) = \frac{\Delta T}{2}$$

$$A(\Omega) = \frac{\Delta T}{2}$$

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1D thermal diff. equ.: oscillating boundary cond.

- Hence the solution to the problem for $x \geq 0$ is

$$T(x, t) = T_0 + \Delta T e^{-x/\delta} \cos\left(\Omega t - \frac{x}{\delta}\right)$$

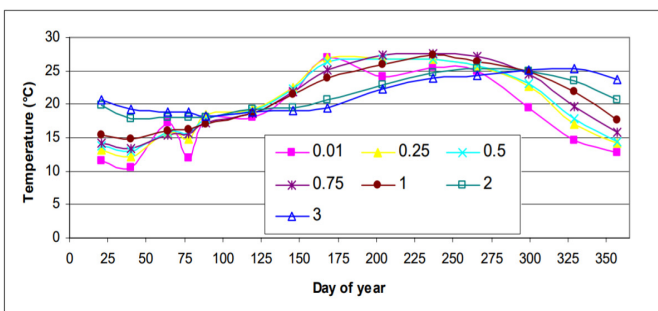
where $\delta = \sqrt{\frac{2D}{\Omega}} = \sqrt{\frac{2\kappa}{\Omega C}}$ is called the **skin depth**.

Some important features:

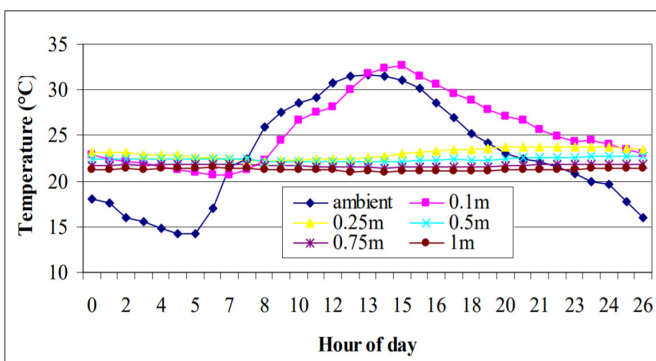
- T falls off exponentially as $e^{-x/\delta}$
- There is a phase shift of x/δ radians in the oscillations.
- $\delta \propto \Omega^{1/2}$, therefore faster oscillations fall off faster.

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Measured daily/annual soil temperature profile



Ground temperature (°C) at various depths at 6:00 hours, during the year 2004



Time lag observed in temperature penetration for 26 May 2004.

$$T(x, t) = T_0 + \Delta T e^{-x/\delta} \cos\left(\Omega t - \frac{x}{\delta}\right)$$

$$\delta = \sqrt{\frac{2D}{\Omega}} = \sqrt{\frac{2\kappa}{\Omega C}}$$

Note:

(1) Phase shift increasing with depth in data, as predicted

(2) Skin depth theoretically $\sqrt{365} = 19$ x more for annual as opposed to daily temperature variation. From figure $\delta_{\text{year}} \approx 4\text{m}$, $\delta_{\text{day}} \approx 0.12\text{m}$, suggests some change in D with depth

Thermal Diffusion Equation: Steady State

Steady State

- Once a steady state is reached, the system will no longer depend on time. Hence, $\partial T / \partial t = 0$
- In this case the thermal diffusion equation reduces to a **Laplace equation**

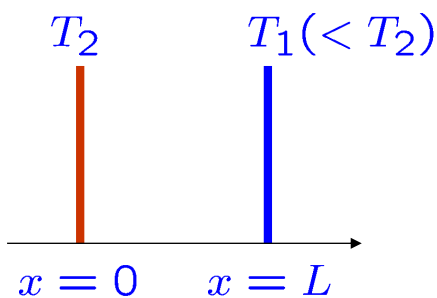
$$\Delta T = \nabla^2 T = 0$$

Note:

The thermal diffusivity $D = \kappa / C$ plays no role in this equation, although there is still a heat flux - $\kappa \nabla T$. Hence, the thermal conductivity κ is still relevant.

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Example



Consider two parallel planes at two different temperatures and a distance L apart.

- Find the heat flux in the steady state.
- Steady state implies that we need to use the 1D Laplace equation

$$\partial^2 T / \partial x^2 = 0$$

- Integrating twice and inserting the boundary conditions yields

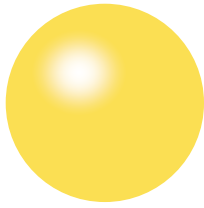
$$T = \frac{(T_1 - T_2)x}{L} + T_2 \quad \text{for} \quad 0 \leq x \leq L$$

- The heat flux is then $J = -\kappa \left(\frac{\partial T}{\partial x} \right) = \frac{\kappa}{L} (T_2 - T_1)$.

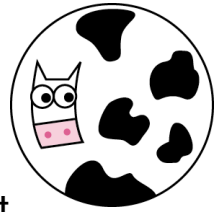
κ/L is called the **thermal conductance**, measured in $\text{Wm}^{-2}\text{K}^{-1}$. Its inverse is known as **thermal resistance**.

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Thermal Diff. Equ. for Spherical Symmetry



- Often we have to deal with problems with spherical symmetry.
- Typical examples are planets and stars, but also a cow could be regarded to first approximation as a sphere.



- Hence, we need to use the Laplace operator in spherical coordinates:

$$\nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2}$$

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Thermal Diff. Equ. for Spherical Symmetry

- Therefore, a spherical object that conducts heat isotropically in all directions (meaning T is only a function of r) the 3D Laplace operator $\Delta T = \nabla^2 T$ reduces to

$$\nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right)$$

- And the diffusion equation becomes

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right)$$

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3D Thermal Diff. Equ. - Example

Consider a sphere conducting heat under steady state conditions:

- Steady state means $\partial T / \partial t = 0$
- Our diffusion equation reduces then to the Laplace equation

$$\Delta T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0$$

- A general solution to this differential equation is

$$T = A + \frac{B}{r}$$

where **A** and **B** are constants.

Notice the analogy to the Laplace equation in electromagnetism. There the Coulomb potential of a charge also falls off as $1/r$.

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Final Remarks (1)

- Classical Thermodynamics gives us 4 important laws (based on observations) for thermal many particle systems:
 - 0th law** \longrightarrow Temperature **T**
 - 1st law** \longrightarrow Energy **U**, which is conserved
 - 2nd law** \longrightarrow Entropy **S**, which can only rise for a change in an isolated multiparticle system.
 - 3rd law** \longrightarrow Gives us a numerical value for **S**; also: it tells us we can not attain zero Kelvin.

and a master equation that folds the concepts and constraints of the laws of classical thermodynamics into one expression:

$$dU = TdS - pdV (+\mu dN)$$

- For isolated systems, the entropy (defined by $dS = dq_{rev}/T$) rises. For systems linked to 'the environment' you have to also consider the entropy change of the environment and this is done with the assistance of thermodynamic potentials.
- Statistical mechanics then provides us with a link between the molecular motions and the macroscopic properties, and an understanding of the 'reason why'

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Final Remarks (2)

- 2nd law: 'The direction of an irreversible process is a function of the states of the system' – i.e. if a change is irreversible, then it is irreversible unless you do work to push it back – in which case something somewhere else is paying.
- Any multi-particle process that achieves a definite result must be irreversible.
- The reason why you cannot find a process that beats the second law is based on the time reversibility of the laws of dynamics. If you try and shift equilibrium by speeding up the forward paths, this must also speed up the reverse ones, otherwise you could tell which way to run the film.
- Irreversible process occur when a constraint is moved enabling access to previously un/under occupied microstates in a context where we are making no attempt at reversing the microscopic motions of a system, but just letting them propagate forwards, allowing the system to 'spread out' across the accessible microstates.
- The probability of the system being in a particular microstate converges to the average as equilibrium is established. Classical thermodynamics stumbled upon a recipe for working out changes in the log of the time average geometric mean of the state probabilities ($dS = dQ_{rev}/T = -k d \log p_{TAGM} = -k d(\sum_i p_i \log p_i)$). p_{TAGM} drops monotonically as a uniform microstate probability is approached, so the this 'entropy' they hit on rises.
- If a system is in thermal equilibrium with a constant temperature 'reservoir', the probability of it being in a microstate of energy is given by a Boltzmann factor, which then becomes central to working out the properties of such systems.

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The End

