

Non-equilibrium thermodynamics

Background to NEMD simulations

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Contents

Lecture 1 - Basics

Balance equations

Local equilibrium approximation

Entropy balance

Entropy production

Linear constitutive relations and transport coefficients

Curie's principle

Lecture 2 - Extensions

Multicomponent systems

- Soret & Dufour effects

Angular momentum

- Spin coupling

Nonlinear constitutive relations

- Heat flow under strong shear



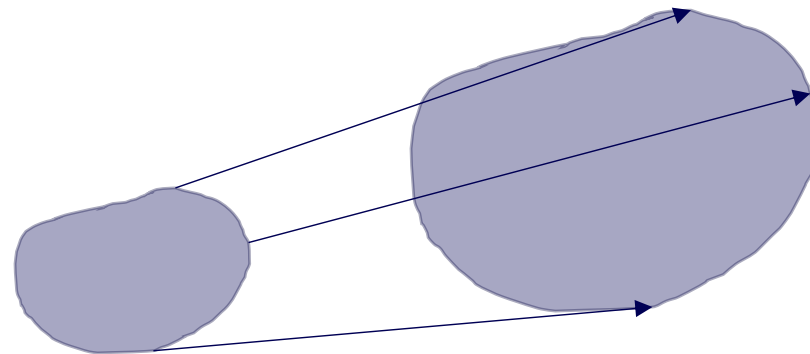
Rate of change of a quantity

Total rate of change of X in the co-moving volume V .

$$\frac{dX}{dt} = \frac{d}{dt} \int_{V(t)} \rho x dV$$

Density of x (amount of x per unit volume)
 x = specific x (x per unit mass)

Note: points on the boundary of the volume $V(t)$ are moving at the local streaming velocity \mathbf{v} .



Reynolds transport theorem

$$\begin{aligned} \frac{d}{dt} \int_{V(t)} \rho x dV &= \int_V \frac{\partial (\rho x)}{\partial t} dV + \int_A \rho x \mathbf{v} \cdot d\mathbf{A} \\ &= \int_V \left[\frac{\partial (\rho x)}{\partial t} + \nabla \cdot (\rho x \mathbf{v}) \right] dV \\ &= \int_V \rho \frac{dx}{dt} dV \\ &= \int_V [-\nabla \cdot \mathbf{J}_x + \sigma_x] dV \end{aligned}$$

Rate of change of X with V fixed

Rate of change of X due to the motion of V

Use the divergence theorem

Use the relation between total and partial derivatives

Physically, the amount of X in a comoving V can only change by diffusive flux and production



Eulerian and Lagrangian balance equations

Combining the last three lines, we have

$$\begin{aligned}\int_V \left[\frac{\partial(\rho x)}{\partial t} + \nabla \cdot (\rho x \mathbf{v}) \right] dV &= \int_V \rho \frac{dx}{dt} dV \\ &= \int_V [-\nabla \cdot \mathbf{J}_x + \sigma_x] dV\end{aligned}$$

Since these apply for ANY volume, including a vanishingly small one, they also apply at a point

Eulerian derivative

$$\frac{\partial(\rho x)}{\partial t} + \nabla \cdot (\rho x \mathbf{v}) = \rho \frac{dx}{dt} = -\nabla \cdot \mathbf{J}_x + \sigma_x$$

Lagrangian derivative

Diffusive transport

Production



Balance equations

Mass balance

$x = \text{specific mass} = 1$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

OR $x = \text{specific volume} = 1/\rho$

$$\nabla \cdot \mathbf{v} = -\frac{1}{\rho} \frac{d\rho}{dt}$$

Exercise: verify these equations

Momentum balance

$x = \text{specific momentum} = \mathbf{v}$

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}^e$$

Internal energy balance

$x = \text{specific internal energy} = u$

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho u \mathbf{v}) = \rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q - \mathbf{P}^T : \nabla \mathbf{v}$$



Entropy balance

Entropy balance

$x = \text{specific entropy} = s$

$$\frac{\partial (\rho s)}{\partial t} + \nabla \cdot (\rho s \mathbf{v}) = \rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s$$

Entropy flux

Entropy production

↑

Rate of change of entropy density at a fixed point

↖

Rate of change of entropy density due to convection

↖

Rate of change of entropy density at a co-moving point

Local equilibrium – Gibbs equation

We need another equation for the entropy.

Equilibrium thermodynamics

Reversible change – total (extensive)

$$dU = TdS - pdV + \mu dM$$

Reversible change – local (material element with fixed M)

$$du = Tds - pdv$$



Entropy balance

Entropy change

For each small material element, assume that the entropy change obeys the Gibbs equation.

$$du = Tds - pdv$$

$$du = Tds - pd \left(\frac{1}{\rho} \right)$$

$$\frac{\rho}{T} \frac{du}{dt} = \rho \frac{ds}{dt} + \frac{p}{\rho T} \frac{d\rho}{dt}$$

Entropy change

Now eliminate the total derivative of the entropy.

$$\begin{aligned} \rho \frac{ds}{dt} &= \frac{\rho}{T} \frac{du}{dt} - \frac{p}{\rho T} \frac{d\rho}{dt} \\ &= -\nabla \cdot \mathbf{J}_s + \sigma_s \end{aligned}$$

Use the energy and mass balance equations in the right hand side.



Entropy balance

Entropy change

Equate the two expressions for the rate of entropy change

$$\frac{\rho}{T} \frac{du}{dt} - \frac{p}{\rho T} \frac{d\rho}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s$$
$$-\frac{1}{T} \nabla \cdot \mathbf{J}_q - \frac{1}{T} \mathbf{P}^T : \nabla \mathbf{v} + \frac{p}{T} \nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{J}_s + \sigma_s$$

Now express the lhs in terms of a divergence and non-divergence term so that the entropy flux and entropy production can be identified.



Entropy balance

Heat flux

The heat flux term can be written in terms of a simple divergence by using

$$\nabla \cdot \left(\frac{\mathbf{J}_q}{T} \right) = \frac{1}{T} \nabla \cdot \mathbf{J}_q - \frac{\mathbf{J}_q}{T^2} \cdot \nabla T$$

Pressure tensor

The pressure can be divided into equilibrium and nonequilibrium parts

$$\mathbf{P} = \mathbf{\Pi} + p\mathbf{1}$$

Nonequilibrium pressure Local equilibrium pressure

So the thermodynamic work due to deformation can also be simplified as

$$\mathbf{P}^T : \nabla \mathbf{v} = \mathbf{\Pi}^T : \nabla \mathbf{v} + p \nabla \cdot \mathbf{v}$$



Entropy balance

Entropy flux and entropy production

Substitute the previous results into the entropy balance equation

$$\begin{array}{ccc}
 \text{Entropy transfer} & \text{Entropy production} & \text{1/T x Reversible work} \\
 \boxed{-\nabla \cdot \left(\frac{\mathbf{J}_q}{T} \right)} & \boxed{-\frac{\mathbf{J}_q}{T^2} \cdot \nabla T - \frac{1}{T} \boldsymbol{\Pi}^T : \nabla \mathbf{v}} & \boxed{-\frac{p}{T} \nabla \cdot \mathbf{v} + \frac{p}{T} \nabla \cdot \mathbf{v}} = -\nabla \cdot \mathbf{J}_s + \sigma_s \\
 & & = 0
 \end{array}$$

This allows us to identify

$$\mathbf{J}_s = \frac{\mathbf{J}_q}{T} \quad \text{Entropy flux}$$

$$\sigma_s = -\frac{\mathbf{J}_q}{T^2} \cdot \nabla T - \frac{1}{T} \boldsymbol{\Pi}^T : \nabla \mathbf{v} \quad \text{Entropy production}$$



Linear constitutive equations

Thermodynamic fluxes and forces

The entropy production is in the form of a bilinear function of the thermodynamic fluxes and their driving forces

$$\sigma_s = -\frac{\mathbf{J}_q}{T^2} \cdot \nabla T - \frac{1}{T} \mathbf{\Pi}^T : \nabla \mathbf{v}$$

Linear constitutive relations

Assume that the fluxes are linear functions of the thermodynamic forces

$$\mathbf{J}_i = \sum_j \mathbf{X}_j \cdot \frac{\partial \mathbf{J}_i}{\partial \mathbf{X}_j} + \dots$$



Linear constitutive equations

Curie's principle

For isotropic materials, the material property tensors must be isotropic tensors.

The fluxes are either polar or axial vectors.

These two facts limit couplings in the linear regime, so that fluxes can only depend on thermodynamic forces with the same tensor characteristics.

Vectors couple to vectors

Scalars couple to scalars – etc.

Fourier's law – heat flow

The heat flux can only depend on the temperature gradient (**one component**).

$$\begin{aligned}\mathbf{J}_q &= -L_q \frac{1}{T^2} \nabla T \\ &= -\lambda \nabla T\end{aligned}$$



Linear constitutive equations

Viscous flow

The entropy production due to viscous flow can be further decomposed into its irreducible components:

$$\mathbf{\Pi}^T : \nabla \mathbf{v} = \Pi \nabla \cdot \mathbf{v} + \mathbf{P}^{ts} : (\nabla \mathbf{v})^{ts}$$

Where we have omitted the antisymmetric part.

Newton's law – shear viscosity

Traceless symmetric velocity gradient corresponds to shear deformation:

$$\mathbf{P}^{ts} = -2\eta (\nabla \mathbf{v})^{ts}$$

Stokes' law – bulk viscosity

Scalar velocity gradient corresponds to bulk (isotropic) deformation:

$$\Pi = -\eta_v \nabla \cdot \mathbf{v}$$

