TD 1: Some Irreversible Processes - Solutions

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1   Basics of Diffusion.   We consider the transport of charges, particles and thermal energy. We denote $\mathbf{j}_q$, $\mathbf{j}_n$ and $\mathbf{j}_U$ the associated currents and ρ_q, ρ_n and ρ_U the associated densities.

1. What are the three ways of transports of heat? Describe their physical origins.

2. Remind Ohm's law, Fick's law and Fourier's law. Comment the differences.

3. What phenomenological approach leads to these laws.

4. Give the name, the dimension and an order of magnitude of the three phenomenological coefficients.

5. We introduce the creation rate by unit volume for each quantity: τ_q, τ_n and τ_U. What can be the physical origin of these rates?

6. What physical principle can be used to get a diffusion equation for each of these quantities? Obtain these equations for temperature and particle density.

7. Find the relaxation equation of the charge.

8. What difference is there between these different processes? What are the scale laws or typical scales for these phenomena?

9. How would these equations be modified in the presence of a drift? In what physical context does this happen?

10. What other diffusion phenomenon do you know?

Correction

1. Diffusion: exchange of heat using the gradient of temperature without movement. Convection: the gradient of temperature generates a movement of the fluid mixing the temperature. Radiation: through the emission of electromagnetic waves.

2. Ohm's law: $\mathbf{j}_q = \gamma \mathbf{E}$. Fick's law: $\mathbf{j}_n = -D\nabla\rho_n$. Fourier's law: $\mathbf{j}_U = -\lambda\nabla T$. Ohm's law works with the electric field rather than with the charge density, but the electric field is generated by the gradient of charge density. Fourier's law works with the temperature rather than the density of thermal energy, but this comes from the proportionality between this density and temperature in ideal cases.

3. Out-of-equilibrium there are fluxes $\mathbf{j}$ while at equilibrium the density ρ is homogeneous. This hypothesis is then to consider that at first order the flux is proportional in the gradient of the density.

4. γ is the electric conductivity, in S/m. For a metal typically $\gamma \sim 10^7$ usi while for wood for instance $\gamma \sim 10^{-14}$ usi. D is the diffusivity, in m^2/s. For air or water $D \sim 10^{-1}$ usi. λ is the thermal conductivity, in W/mK. For metals typically $\lambda \sim 10^2$ usi while for water for instance $\lambda \sim 10^{-1}$ usi.

5. For the charges or number of particles it may be chemical reactions. For the temperature anything generating heat like nuclear of chemical reactions and electronic waves.

6. We can use the conservation property. Thus,

$$\partial_t\rho_n + \nabla\cdot\mathbf{j}_n = \tau_n \implies \partial_t\rho_n = D\Delta\rho_n + \tau_n \tag{1}$$

$$\partial_t\rho_U + \nabla\cdot\mathbf{j}_U = \tau_U \implies \partial_t T = \frac{\lambda}{\rho C}\Delta T + \frac{\tau_U}{\rho C} \tag{2}$$

where ρ is the mass density and C is the heat capacity.

7. For the charge we use Maxwell-Gauß law: $\nabla\cdot\mathbf{E} = \frac{\rho_q}{\epsilon}$, then:

$$\partial_t\rho_q + \nabla\cdot\mathbf{j}_q = \tau_q \implies \partial_t\rho_q + \frac{\gamma}{\epsilon}\rho_q = \tau_q \tag{3}$$

8. For the charge, not only is there diffusion but the charges interacts electrically while the other processes are interactionless. For pure diffuson there is a scale law $\tau \sim l^2$ while for charge relaxation there is a typical time $\frac{\epsilon}{\gamma}$.

9. If there is a drift, we need to use the transport theorem:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{V(t)} \rho = \int_{V(t)} (\partial_t \rho + \nabla \cdot (\rho \mathbf{v})) \tag{4}$$

if the volume $V(t)$ is transported by the velocity distribution $\mathbf{v}$. Then, the term $\partial_t \rho$ would be replaced by $\partial_t \rho + \nabla \cdot (\rho \mathbf{v})$. This happens in fluid dynamics or for the transport of charges.

10. The viscosity in fluid dynamics.

2   Polymer Diffusion.

In this exercise we work in the microcanonical ensemble and give a basic model to describe a polymer. We consider a chain of N monomers of length a. Each monomer is linked to the previous monomer and present a random angle of uniform probability. We are interested in the total length $\mathbf{L}$ of the polymer.

1. What hypotheses are necessary to get a uniform distribution?

2. What is the expectancy $\mathbb{E}(\mathbf{L})$? What is the mean squared expectancy $L_2 = \sqrt{\mathbb{E}(\mathbf{L}^2)}$? Comment.

3. We denote $\mathbb{P}(s, \mathbf{l})$ the probability to reach the position $\mathbf{l}$ after sN monomers. Find an equation of induction for $\mathbb{P}$.

4. We go to the continuum limit by taking $a \to 0$ and $N \to +\infty$ with fixed L_2. Find a partial differential equation for $\mathbb{P}$. What do you recognize?

5. Solve this equation. Is this result surprising? *(hint: it's a Gaussian)*

6. Calculate the entropy $\mathcal{S}(\mathbf{L})$

7. Calculate $\frac{\partial \mathcal{S}}{\partial \mathbf{L}}$. Give a physical interpretation of this result.

Correction

1. No interaction of contact between the monomers and no electric interactions on the monomers.

2. We may write $\mathbf{L} = a \sum_{i=1}^{N} \mathbf{l}_i$ where the $(\mathbf{l}_i)$ are independent random variables describing the random angles. By linearity of the expectancy we find $\mathbb{E}(\mathbf{L}) = \mathbf{0}$ and $L = \sqrt{\mathbb{E}(\mathbf{L}^2)} = \sqrt{N}a$. The typical length scale is in square root like diffusion.

3. By construction,

$$\mathbb{P}(s + \frac{1}{N}, \mathbf{l}) = \frac{1}{4\pi} \int_{S^2} \mathrm{d}\mathbf{x} \, \mathbb{P}(s, \mathbf{l} - a\mathbf{x}). \tag{5}$$

4. We goes at order $\frac{1}{N}$ which corresponds to order a^2:

$$\mathbb{P}(s, \mathbf{l}) + \frac{1}{N}\partial_s \mathbb{P}(s, \mathbf{l}) = \frac{1}{4\pi} \int_{S^2} \mathrm{d}\mathbf{x} \left(\mathbb{P}(s, \mathbf{l}) - a\mathbf{x} \cdot \nabla \mathbb{P}(s, \mathbf{l}) + \frac{1}{2}a^2 (\mathbf{x} \cdot \nabla)^2 \mathbb{P}(s, \mathbf{l}) \right). \tag{6}$$

The term in a vanishes by symmetry. The term $(\mathbf{x} \cdot \nabla)^2$ becomes a Laplacian since the cross terms vanish by symmetry. Finally we find a diffusion equation:

$$\partial_s \mathbb{P}(s, \mathbf{l}) = \frac{1}{6} L_2^2 \Delta \mathbb{P}(s, \mathbf{l}). \tag{7}$$

5. We check that the solution is

$$\mathbb{P}(s, \mathbf{l}) = \left(\frac{1}{6\pi s L_2^2} \right)^{\frac{3}{2}} e^{-\frac{\mathbf{l}^2}{6s L_2^2}} \tag{8}$$

then

$$\mathbb{P}(\mathbf{L}) = \left(\frac{1}{6\pi L_2^2} \right)^{\frac{3}{2}} e^{-\frac{\mathbf{L}^2}{6 L_2^2}}. \tag{9}$$

This is natural to get such a Gaussian because it is the central limit theorem.

6. The probability is proportional to the number of configuration because we are in the microcanonical ensemble. Then, using Boltzmann formula we find up to a constant:

$$\mathcal{S}(\mathbf{L}) = -k_B \frac{\mathbf{L}^2}{6 L_2^2}. \tag{10}$$

7. We calculate

$$\frac{\partial \mathcal{S}}{\partial \mathbf{L}} = -k_B \frac{1}{3 L_2^2} \mathbf{L}. \tag{11}$$

The length being conjugated with the force, this is an entropic force which applies on the polymer generating a harmonic oscillator. Physically, this is the friction caused by thermal noise which pushes the polymer to its state of maximal entropy, when $\mathbf{L} = \mathbf{0}$.

3   Shock Waves.   We consider a compressible perfect fluid of mass density ρ, velocity field $\mathbf{v}$ and pressure field P.

1. Remind the Euler equations for the fluid. Is this set of equations enough to close the system?

2. We suppose that the process is reversible and adiabatic. Deduce an additional equation for the entropy density s per unit mass.

3. We denote ϵ the internal energy density per unit mass. What is the relation between s and ϵ?

4. We denote e the total energy density. Give its expression.

5. Demonstrate that
$$\partial_t e + \nabla \cdot ((e + P)\mathbf{v}) = 0. \tag{12}$$

6. Deduce that when the flow is stationary, $h_{eff} = \epsilon + \frac{1}{2}\mathbf{v}^2 + \frac{P}{\rho}$ is preserved along the lines of current.

7. What is the velocity of sound c_s? Give its expression.

8. We define the Mach number as $Ma = \frac{v}{c_s}$. Discuss what happens when Ma becomes larger than 1. Make figures.

9. In what follows we consider a stationary fluid and follow a line going from $Ma > 1$ to $Ma < 1$. Show that
$$\frac{\mathrm{d}(\rho u)}{\mathrm{d}u} = \rho(1 - Ma^2). \tag{13}$$

10. Plot ρu as a function of u and comment.

    In practice the velocity of sound is dependent of u. We denote it $c(u)$ and the Mach number is $\frac{u}{c(u)}$. We denote with a star (like u^*) the properties at $Ma = 1$ and $Ma^* = \frac{u}{c^*}$. We remind that for a polytropic perfect gas $c^2 = \gamma RT$ and its enthalpy is $\epsilon + \frac{P}{\rho} = C_P T = \frac{c^2}{\gamma - 1}$. We now consider such a gas.

11. Give a relation between Ma and Ma^*. Comment the case $Ma \to +\infty$.

12. Give 3 laws of conservation through the interface $Ma = 1$.

    When the line goes across the sound wall the Prandtl law applies: $u_1 u_2 = c^{*2}$. From these laws specified for the polytropic perfect gas one may calculate
$$\frac{P_2}{P_1} = 1 + \frac{2\gamma}{\gamma + 1}(Ma_1^2 - 1) \quad \text{and} \quad \frac{T_2}{T_1} = \left(1 + \frac{2\gamma}{\gamma + 1}(Ma_1^2 - 1)\right)\frac{2 + (\gamma - 1)Ma_1^2}{(\gamma + 1)Ma_1^2}. \tag{14}$$

13. Calculate the entropy shift $s_2 - s_1$. Comment.

Correction

1. The Euler equations are
$$(\partial_t + \mathbf{v} \cdot \nabla)\rho = -\rho \nabla \cdot \mathbf{v} \quad \rho(\partial_t + \mathbf{v} \cdot \nabla)\mathbf{v} = -\nabla P. \tag{15}$$

    The system is not closed between there is no constraint on P. We need an equation of state an thermodynamic evolution equation.

2. s is conserved so that
$$(\partial_t + \mathbf{v} \cdot \nabla)s = 0. \tag{16}$$

3. The thermodynamic identity $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ becomes $\mathrm{d}\epsilon = T\mathrm{d}s + \frac{P}{\rho^2}\mathrm{d}\rho$.

4. We total energy is $e = \rho\epsilon + \frac{1}{2}\rho\mathbf{v}^2$.

5. The evolution of e is
$$(\partial_t + \mathbf{v} \cdot \nabla)e = \epsilon(\partial_t + \mathbf{v} \cdot \nabla)\rho + \rho T(\partial_t + \mathbf{v} \cdot \nabla)s + \frac{P}{\rho}(\partial_t + \mathbf{v} \cdot \nabla)\rho + \frac{1}{2}\mathbf{v}^2(\partial_t + \mathbf{v} \cdot \nabla)\rho \tag{17}$$
$$+ \rho\mathbf{v} \cdot (\partial_t + \mathbf{v} \cdot \nabla)\mathbf{v} \tag{18}$$
$$= \frac{e + P}{\rho}(\partial_t + \mathbf{v} \cdot \nabla)\rho - \mathbf{v} \cdot \nabla P. \tag{19}$$

    One easily checks that developing the expected result gives the same expression.

6. We have $\nabla \cdot ((e + P)\mathbf{u}) = \nabla \cdot (h_{eff}\rho\mathbf{v}) = 0$ and from Euler equations $\nabla \cdot (\rho\mathbf{v}) = 0$. Thus, $\mathbf{v} \cdot \nabla h_{eff} = 0$.

7. This is the velocity of mechanical waves in the fluid. Its expression is $c_s^2 = \frac{1}{\rho_0 \chi_S}$ where ρ_0 is the averaged mass density and χ_S is the compressibility.

8. This is the sound wall: the perturbations accumulates at $Ma = 1$.

9. From Euler equations $u\,\mathrm{d}u = -\frac{\mathrm{d}P}{\rho}$. Thus, $\frac{\mathrm{d}\rho}{\mathrm{d}u} = \frac{\mathrm{d}P}{\mathrm{d}u}\frac{\mathrm{d}\rho}{\mathrm{d}P} = -\frac{\rho}{u}\rho\chi_S = -\frac{\rho u}{c_s^2}$. Then, $\frac{\mathrm{d}(\rho u)}{\mathrm{d}u} = \rho - \rho\frac{u^2}{c_s^2} = \rho(1 - Ma^2)$. After $Ma = 1$ when u increases ρu decreases so that the density becomes very low.

10. We use that $h_{eff} = \frac{1}{2}u^2 + \frac{c^2}{\gamma-1}$ is preserved. The comparison with the state at $Ma = 1$ gives

$$\frac{1}{2} + \frac{1}{(\gamma-1)Ma^2} = \left(\frac{1}{2} + \frac{1}{(\gamma-1)}\right)\frac{1}{Ma^{*2}} \implies Ma^{*2} = \frac{\gamma+1}{\gamma-1+\frac{2}{Ma^2}}. \tag{20}$$

When $Ma \to +\infty$ then $Ma^* \to \sqrt{\frac{\gamma+1}{\gamma-1}}$ so that u is upper bounded.

11. Conservation of mass: $\rho_1 u_1 = \rho_2 u_2$. Conservation of momentum: $\rho_1 u_1^2 + P_1 = \rho_2 u_2^2 + P_2$. Conservation of energy: $h_{eff,1} = h_{eff,2}$.

12. We use the thermodynamic identity $\mathrm{d}h = T\mathrm{d}s + \frac{1}{\rho}\mathrm{d}P$ i.e.

$$\mathrm{d}s = \frac{\mathrm{d}h}{T} - \frac{\mathrm{d}P}{\rho T} = C_P\frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}P}{P} \implies s_2 - s_1 = C_P\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right). \tag{21}$$

Thus,

$$s_2 - s_1 = C_v\ln\left(1 + \frac{2\gamma}{\gamma+1}(Ma_1^2 - 1)\right) + C_P\ln\left(\frac{2 + (\gamma-1)Ma_1^2}{(\gamma+1)Ma_1^2}\right). \tag{22}$$

This cannot be negative so that Ma_1 cannot be too small. Since we may choose anywhere on the line we conclude that $Ma_1 > 1$ and then $Ma_2 < 1$. There can be a sound wall only from $Ma > 1$ to $Ma < 1$. Moreover, we see that there is a production of entropy which is natural since a sound wall is all but an equilibrium. However we remember that we included no dissipation and supposed the flow to be reversible and adiabatic. Understanding properly the origin of this entropy is an open question.