ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

RESCIF
Réseau d'excellence des sciences de l'ingénieur de la Francophonie

Thermodynamique

Relations phénoménologiques linéaires

UCL Université catholique de Louvain

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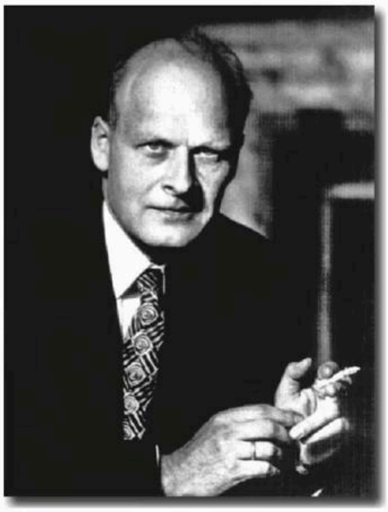
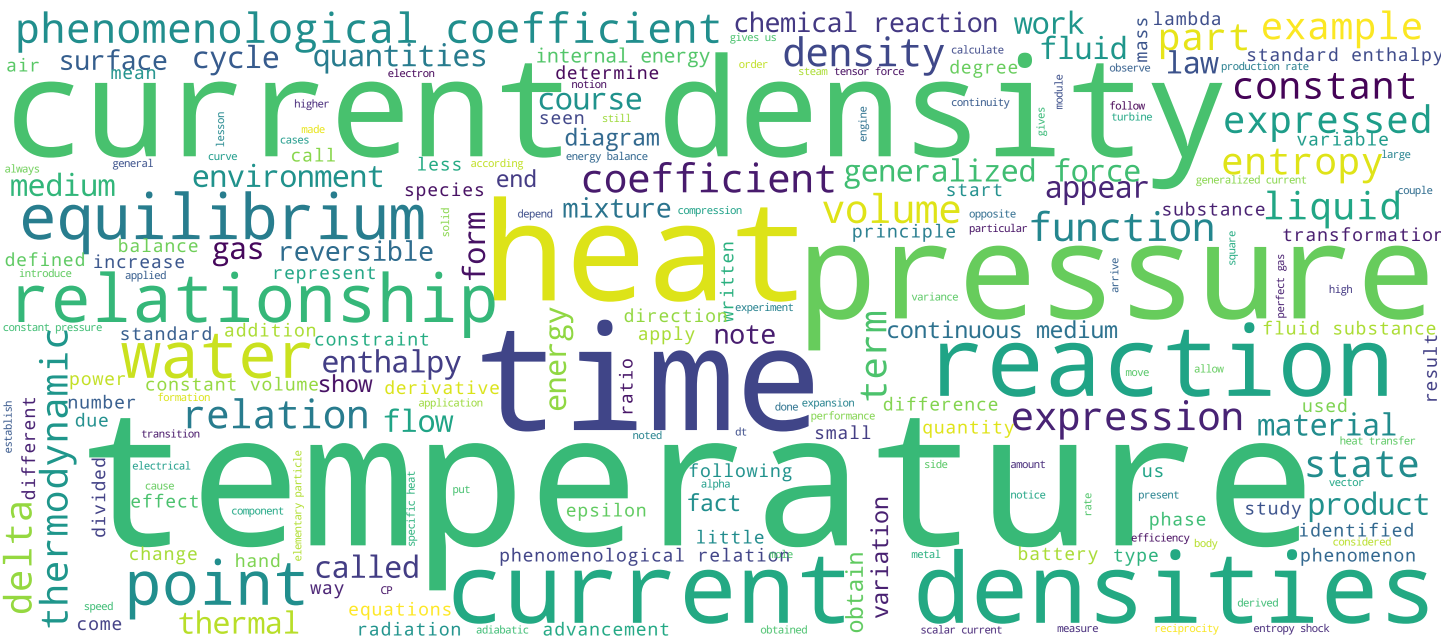


Lars Onsager



Video

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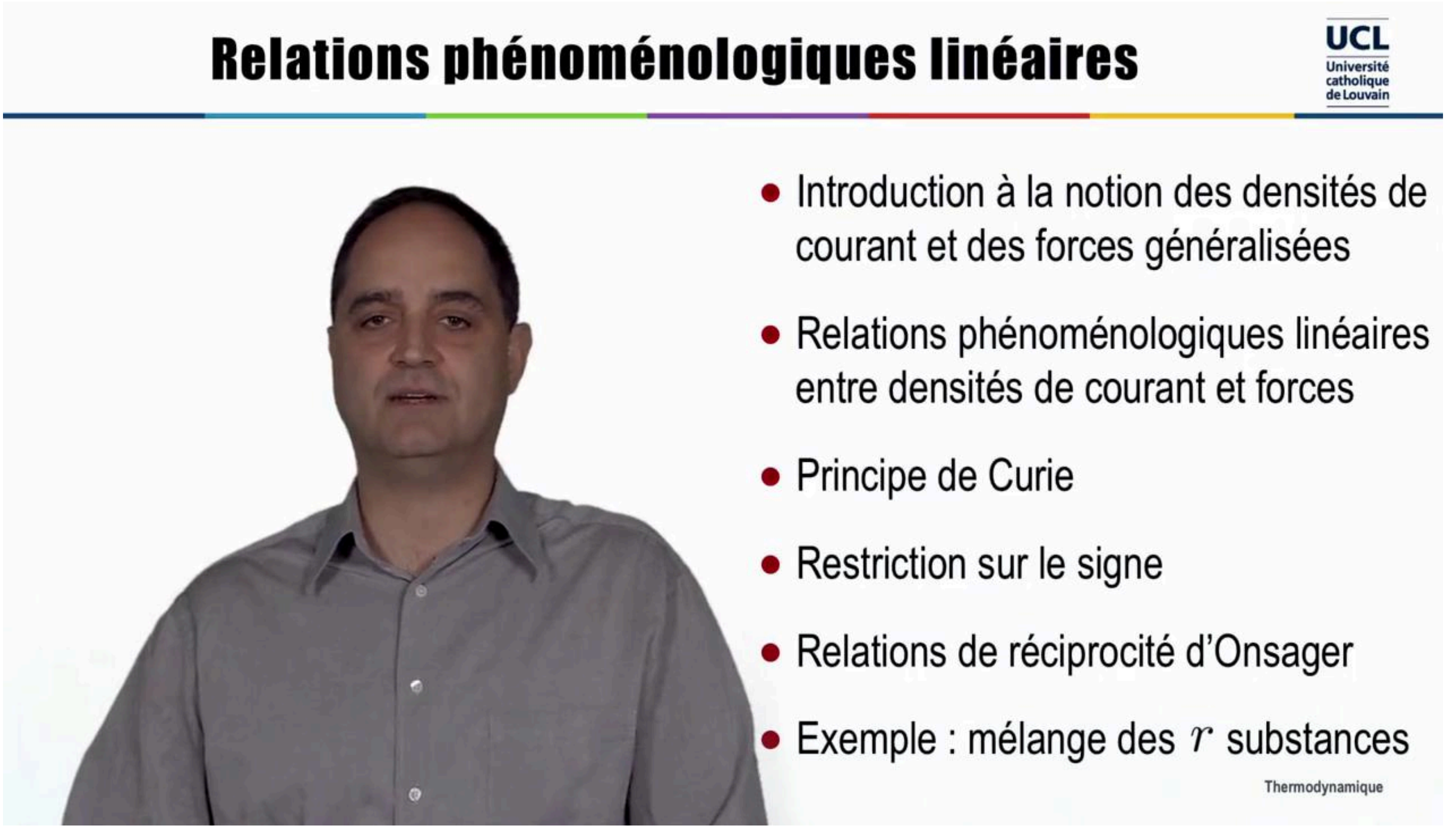
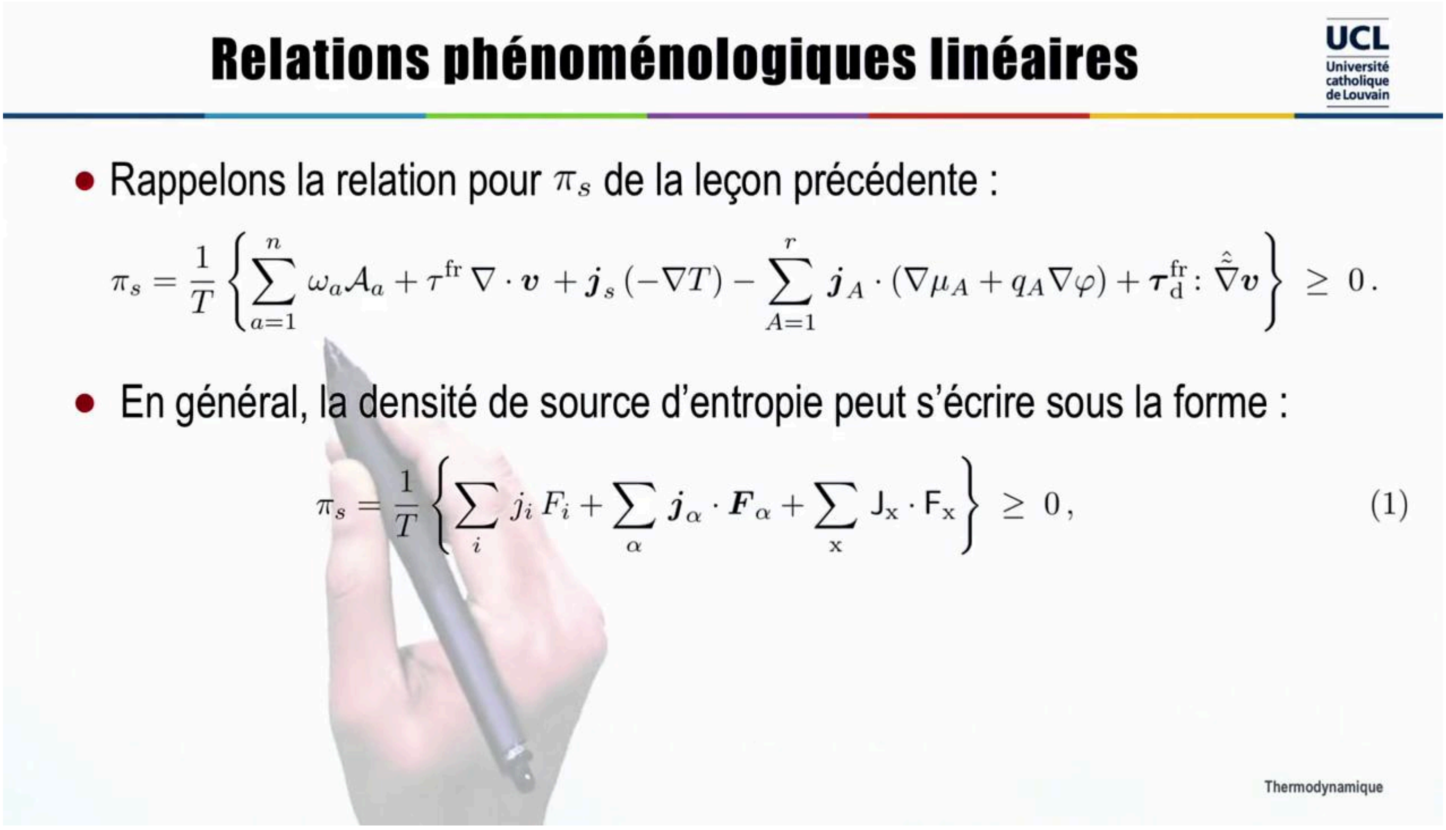


Hello and welcome to the courses of thermodynamics in the previous presentation. We have carried out the energy balance of the continuous medium and we obtained a relation for the density of entropy sulphur of the medium in this part of the course. We elaborate more on this relationship and furthermore, using this relation, we will establish a formalism thermodynamics for the study of processes in equilibrium. The structure of our presentation is as follows. First, we introduce the notion of current density and generalized forces. Then, we deliver relationships linear phenomenology between current density and generalized force, and we will see that this relationship is subject to certain constraints. This constraint is expressed by the Curie principle, by the restriction under wisteria and by the relations of reciprocity of war. Finally, we will apply this thermodynamic formalism to a continuous medium that is made up of fluid substances.

Notes

Summary

0m 05s



First, we recall the relation for the entropy sulfur density, piece that we derived from the previous one. First, we call it the for the entropy sulfur density, part of an air mixture adjoining that that we derived in the previous lesson. We observe that the density of sulfur entropy is expressed as a sum of products. In addition, every product that appears in this relation expresses the rate of entropy production within of the system due to a specific irreversible process. For example, these terms express the production rate of entropy within the system due to chemical reactions. This term expresses the production rate of entropy of the medium due to the viscous pressure. This term expresses the production rate entropy due to thermal diffusion, etc. In general, for a continuous medium, the strain density of entropy can be expressed in the following form. It is expressed as a sum of products. The quantities that appear in these products are classified in two categories. The quantities of the first category are identified as the generalized current densities. For a mixture of fluid substances. This amount are.

Notes

Summary

1m 08s

Relations phénoménologiques linéaires

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- Rappelons la relation pour π_s de la leçon précédente :

$$\pi_s = \frac{1}{T}\left\{\sum_{a=1}^{n} \omega_a \mathcal{A}_a + \tau^{\mathrm{fr}}\,\nabla\cdot\boldsymbol{v} + \boldsymbol{j}_s\,(-\nabla T) - \sum_{A=1}^{r} \boldsymbol{j}_A\cdot(\nabla\mu_A + q_A\nabla\varphi) + \boldsymbol{\tau}_{\mathrm{d}}^{\mathrm{fr}} : \hat{\tilde{\nabla}}\boldsymbol{v}\right\} \geq 0\,.$$

- En général, la densité de source d'entropie peut s'écrire sous la forme :

$$\pi_s = \frac{1}{T}\left\{\sum_i j_i\,F_i + \sum_\alpha \boldsymbol{j}_\alpha\cdot\boldsymbol{F}_\alpha + \sum_{\mathsf{x}} \mathsf{J}_{\mathsf{x}}\cdot\mathsf{F}_{\mathsf{x}}\right\} \geq 0\,, \qquad (1)$$

- $j_i\,, F_i$: densités de courant et forces généralisées scalaires,
- $\boldsymbol{j}_\alpha, \boldsymbol{F}_\alpha$: densités de courant et forces généralisées vectorielles,
- $\mathsf{J}_{\mathsf{x}}\,,\, \mathsf{F}_{\mathsf{x}}$: densités de courant et forces généralisées tensorielles.

Thermodynamique

Method, chemical reaction, pressure since the current density entropy, the current density of substance chemical and the catholic part of the friction tensor. The quantities of the second category are identified as strength generalized for a mixture of fluid substances. This quantity are the affinities of chemical reactions as well as themes that involve clients of its thermodynamic state. In addition, the current densities and the generalized background are classified according to their tensor order. We then have j and f i which represent respectively the current densities and scalar generalized forces G alpha and f alpha which represent the current densities respectively. A generalized force with the and finally we have X and FX which represent respectively the density current and generalized tensor force.

Notes

Summary

2m 33s

Relations phénoménologiques linéaires

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- A l'équilibre, les valeurs de toutes les densités de courant et de toutes les forces sont égales à zéro : $j_i^{\text{eq}} = 0\,, \quad F_i^{\text{eq}} = 0$ etc.

- Nous considérons que les densités de courant généralisées sont des fonctions des forces généralisées : $j_i = j_i\,(F_j,\, \boldsymbol{F}_\alpha,\, \mathsf{F}_{\text{x}})$ etc.

- Nous développons ces fonctions en série de Taylor au voisinage d'un état d'équilibre, en approximant au 1er ordre :

$$j_i = \cancelto{0}{j_i^{\text{eq}}} + \sum_j \left(\frac{\partial j_i}{\partial F_j}\right)^{\text{eq}} (F_j - \cancelto{0}{F_j^{\text{eq}}}) + \dots$$

$$+ \sum_\alpha \left(\frac{\partial j_i}{\partial \boldsymbol{F}_\alpha}\right)^{\text{eq}} (\boldsymbol{F}_\alpha - \cancelto{0}{\boldsymbol{F}_\alpha^{\text{eq}}}) + \dots + \sum_{\text{x}} \left(\frac{\partial j_i}{\partial \boldsymbol{F}_{\text{x}}}\right)^{\text{eq}} (\mathsf{F}_{\text{x}} - \cancelto{0}{\mathsf{F}_{\text{x}}^{\text{eq}}}) + \dots\,,$$

Thermodynamique

We note that in balance, the of all current densities of all functions is equal to zero. We then have quasi at equilibrium zero, f i at equilibrium and zero etc. This way, the entropy shock density of the medium is equal to zero at equilibrium. Now we consider that the densities are two generalized force functions. According to this point of view, the fact that generalized induce generalized current. We then have relations of this type of functions. Now we develop these functions in Taylor series in the vicinity of a steady state and in a first order. We then come to the relationships of this type. Now we notice that given that the values of all current densities of all functions is equal to zero at equilibrium, then this term, i.e. this term so that these terms are all equal to zero.

Notes

Summary

3m 36s

Relations phénoménologiques linéaires

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- Nous arrivons alors aux relations linéaires entre les densités de courant et les forces généralisées :

$$j_i = \sum_j L_{ij} F_j + \sum_\alpha L_{i\alpha} \boldsymbol{F}_\alpha + \sum_{\mathsf{x}} L_{i\mathsf{x}} \mathsf{F}_{\mathsf{x}} \,, \tag{2}$$

- Coefficients phénoménologiques :

$$L_{ij} \equiv \left(\frac{\partial j_i}{\partial F_j}\right)^{\mathrm{eq}} , \qquad L_{i\alpha} \equiv \left(\frac{\partial j_i}{\partial \boldsymbol{F}_\alpha}\right)^{\mathrm{eq}} , \qquad L_{i\mathsf{x}} \equiv \left(\frac{\partial j_i}{\partial \mathsf{F}_{\mathsf{x}}}\right)^{\mathrm{eq}} . \tag{3}$$

- *Principe de Curie* : Les causes d'un phénomène ne peuvent pas présenter plus de symétrie que les effets qu'ils provoquent.

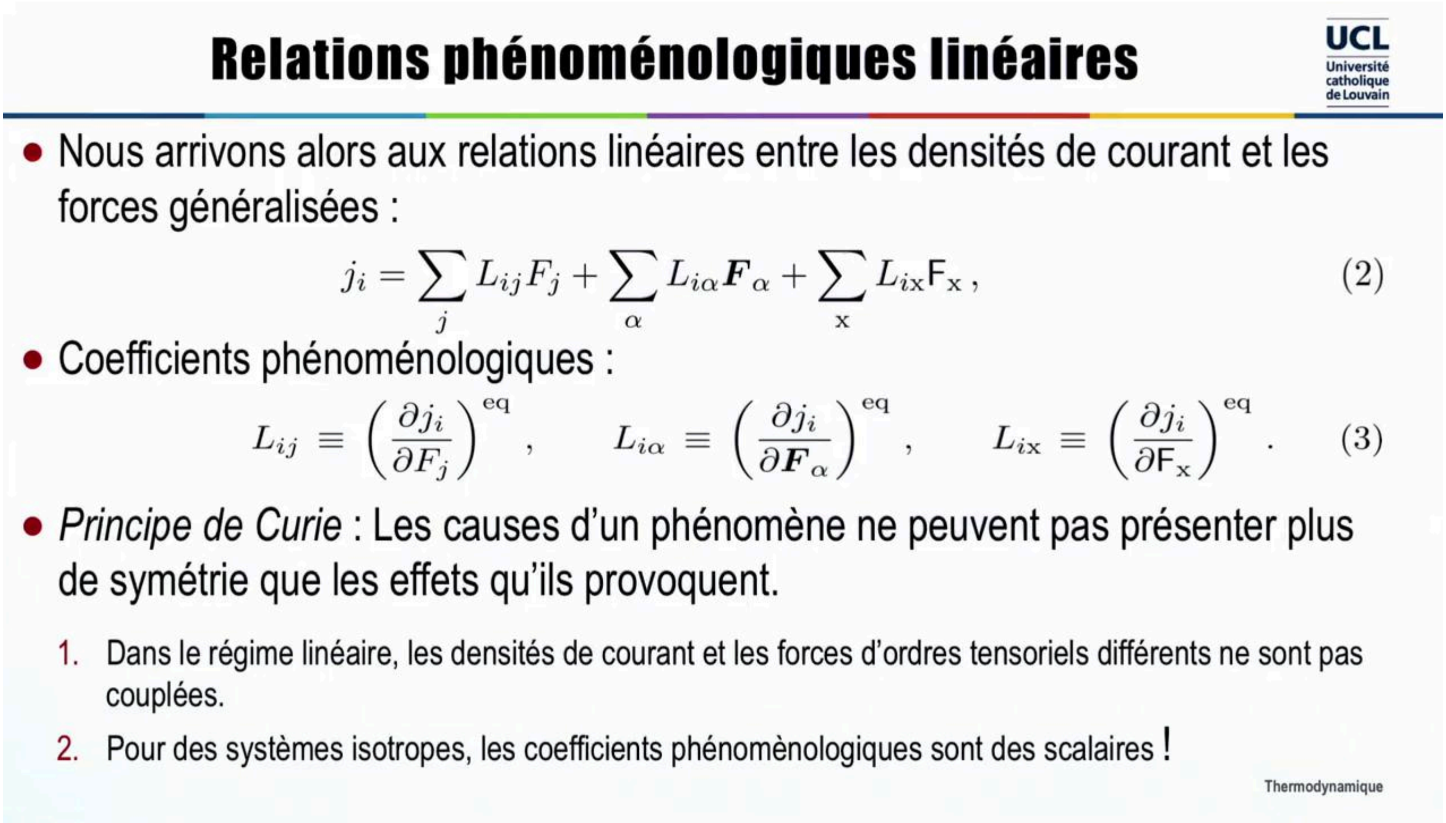
Thermodynamique

We arrive then at the linear relations between current densities and generalized forces. We come to the of this type. The coefficients nj and alpha l x that appear in this relationship are identified as the phenomenological coefficients. According to the expansions. This is the idea that we have considered. The phenomenological coefficients are defined as the partial derivatives of the generalized current densities with respect to the generalized forces at equilibrium. Then is. Phenomenological confusion couple a current density and a generalized force. The tensor wave of coefficients phenomenological dependence of tensor waves. The current density of the force it couples. For example, if a phenomenological coefficient cuts generalized scalar current density with a generalized function scalar, then this coefficient is of scalar character. If a phenomenological coefficient coupled to a current density generalized vector with a generalized force with. Then this coefficient is a tensor. Etc. The phenomenological coefficients are subject to certain constraints. The first constraint is expressed by Curie's principles, which are the following. The causes of a phenomenon cannot be have more symmetry than the effects they cause.

Notes

Summary

4m 42s



This principle applied to linear relations means that in the current densities and different tensor forces do not are not coupled for isotropic systems. We can show this result rigorously by means of a theorem using the tensor representation theorem. They are too linear. Moreover, for isotropic systems in the linear regime, the phenomenological coefficients are scalars.

Notes

Summary

6m 06s

Relations phénoménologiques linéaires

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- Nous arrivons aux relations suivantes entre les densités de courant et les forces :

$$j_i = \sum_j L_{ij} F_j \,, \qquad \boldsymbol{j}_\alpha = \sum_\alpha \mathsf{L}_{\alpha\beta} \boldsymbol{F}_\beta \,, \qquad \mathsf{J}_\mathrm{x} = \sum_\beta \mathbf{L}_\mathrm{xy} \mathsf{F}_\mathrm{y} \,, \tag{4}$$

- A l'aide de ces relations, la densité de source d'entropie s'écrit sous la forme :

$$\pi_s \;=\; \sum_{i,j} L_{ij} F_i F_j \;+\; \sum_{\alpha,\beta} (\mathsf{L}_{\alpha\beta} \boldsymbol{F}_\alpha) \cdot \boldsymbol{F}_\beta \;+\; \sum_{\mathrm{x,y}} (\mathbf{L}_\mathrm{xy} \mathsf{F}_\mathrm{x}) : \mathsf{F}_\mathrm{y} \;\geq\; 0 \,, \tag{5}$$

- *Restriction sur le signe* : la condition $\pi_s \geq 0$ requiert que les matrices des coefficients phénoménologiques, $\{L_{ij}\},\ \{L_{\alpha\beta}\},\ \{L_\mathrm{xy}\}$, soient définies positives :

$$L_{ii} > 0 \,, \qquad L_{ii}\, L_{jj} \geq \tfrac{1}{4}\,(L_{ij} + L_{ji})^2 , \qquad \text{etc.}$$

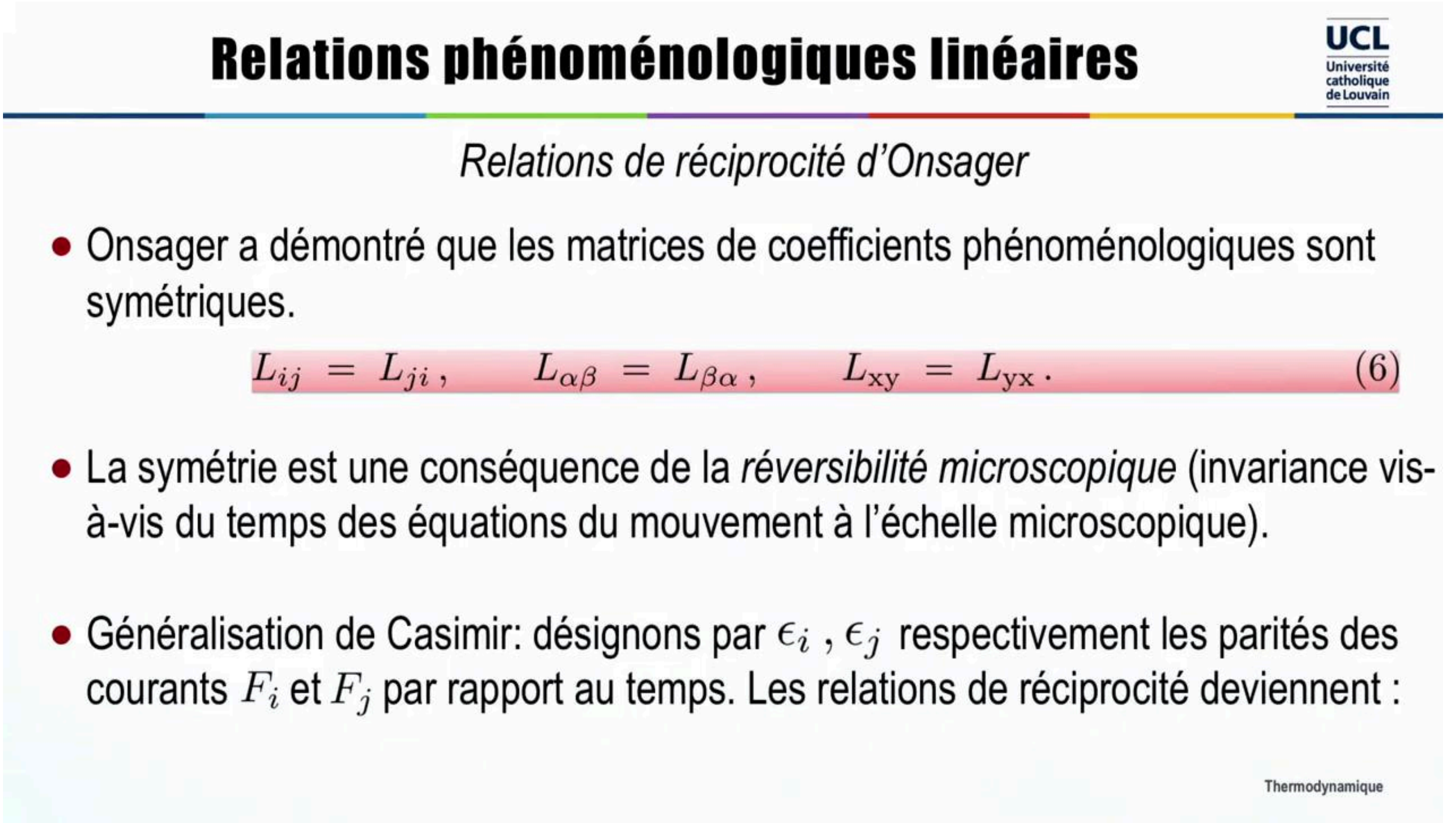
Thermodynamique

We then come to the relationships between the current densities, the generalized forces. We have coupling between current density and scalar generalized strength, decoupling between current density and vector analysis force and coupling between current density and force tensor analysis. Using these relationships. The density of entropy shocks is written in the following form. That is to say that the density of the sources of entropy PS is expressed as a quadratic form. The second principle of thermodynamics imposes an additional constraint on the phenomenological coefficient. We then have the restriction under glycine. The condition that Piet is now negative requires that the matrix of phenomenological coefficients is defined positive for isotropic systems and in the linear regime. These conditions are necessary and sufficient for the non-negativity of the entropy shock density piece. For example, according to this condition, the diagonal terms of matrix of phenomenological coefficients must be positive, etc.

Notes

Summary

6m 38s



Finally, we still have a constraint. This constraint is expressed by the reciprocal relations of which the money was allied in 1939. His war has shown that the matrices of the phenomenological coefficients are symmetrical. We then have this symmetry relation between the phenomenological coefficient. It is Lolo his war. Symmetry is a consequence of microscopic reversibility, i.e. a variance with respect to of the equations of motion at the microscopic scale. To achieve this result, one hardly has to consider generalized current densities that are expressed at the microscopic scale by functions that are evenly matched to of time with respect to the velocities of elementary particles. Then Casimir generalize these results considering, in addition to the current densities which are expressed at the microscopic scale by odd functions vis-a-vis time vis-a-vis the velocities of elementary particles. We then have the generalization of the Casimir. Draw by epsilon i epsilon j respectively the parity of currents f and F said with respect to time. For example, if f i is even with respect to time and with respect to speeds of elementary particles, then epsilon is equal to an.

Notes

Summary

7m 51s

Relations phénoménologiques linéaires

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Relations de réciprocité d'Onsager

- Onsager a démontré que les matrices de coefficients phénoménologiques sont symétriques.

$$L_{ij} = L_{ji}\,, \qquad L_{\alpha\beta} = L_{\beta\alpha}\,, \qquad L_{\mathrm{xy}} = L_{\mathrm{yx}}\,. \tag{6}$$

- La symétrie est une conséquence de la *réversibilité microscopique* (invariance vis-à-vis du temps des équations du mouvement à l'échelle microscopique).

- Généralisation de Casimir: désignons par ϵ_i , ϵ_j respectivement les parités des courants F_i et F_j par rapport au temps. Les relations de réciprocité deviennent :

$$L_{ij} = \epsilon_i \epsilon_j \, L_{ji}\,, \qquad L_{\alpha\beta} = \epsilon_\alpha \epsilon_\beta \, L_{\beta\alpha}\,, \qquad L_{\mathrm{xy}} = \epsilon_{\mathrm{x}} \epsilon_{\mathrm{y}} \, L_{\mathrm{yx}}\,.$$

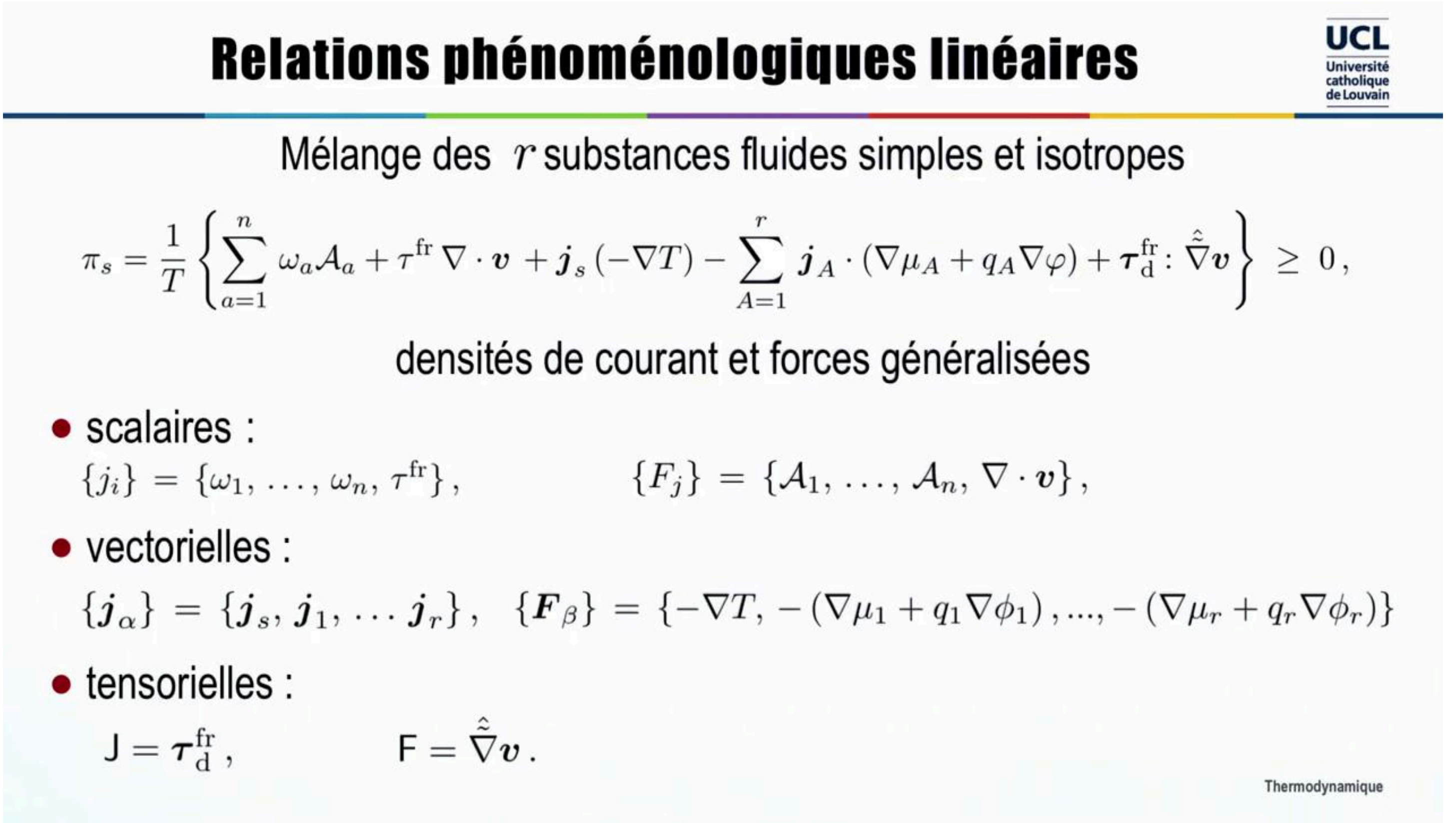
Thermodynamique

If the current density f is odd with respect to time, then. The coefficients epsilon i is equal to fifteen. Reciprocal relationships take this form. For example, we consider phenomenological coefficients it acts and it acts. If these two coefficients a couple of current densities that have the same parity with respect to time with respect to of elementary particle velocities, then these two coefficients phenomenology obey a relation of symmetry. If on the other hand these two coefficients a couple of current density of different parity a, then there will be an anti-symmetry relation between these two coefficients etc.

Notes

Summary

9m 08s



Now we can apply this dynamic formalism to a continuous medium which is a mixture of fluid, simple and isotropic substance. We call it the for the piecewise entropy source density for each medium. First, we will identify and classify the current densities and generalize the scalar current densities are the rates of chemical reactions. And the pressure since the generalized scalar folk sound, chemical reaction affinities and rate divergence. The vector current densities are. The current density of entropy as well as the densities of fluid substance. The fact that generalized and vector are the opposite of the temperature gradient, as well as the opposites of these quantities in parentheses which are identified as the ingredients of the electrochemical potential of the fluid substance. Finally, the tensor current density is the diatonic part of the tensor of friction and the generalized tensor force is the catholic part of the deformation tensor.

Notes

Summary

10m 00s

Relations phénoménologiques linéaires

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- Relations phénoménologiques linéaires pour les densités de courant scalaires :

$$\begin{cases} \omega_a = \sum_b L_{ab}\, \mathcal{A}_b + L_{af}\, \nabla \cdot \boldsymbol{v}\,, \\ \tau^{\,\mathrm{fr}} = \sum_b L_{fb}\, \mathcal{A}_b + L_{ff}\, \nabla \cdot \boldsymbol{v}\,, \end{cases} \tag{7}$$

$$\begin{aligned} L_{ab} &= L_{ba}\,, \qquad a,\, b = 1, \ldots, n\,, \\ L_{af} &= -L_{fa}\,, \qquad a = 1, \ldots, n\,. \end{aligned} \tag{8}$$

Thermodynamique

These are the phenomenological relations linear for scalar current densities. In addition, we have this relationship of reciprocity concerning the phenomenological coefficient that appears in this phenomenological relation according to the relations of reciprocity. It a b is equal to l b.a while l to f is equal to l f a.

Notes

Summary

11m 12s

Relations phénoménologiques linéaires

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- Relations phénoménologiques linéaires pour les densités de courant vectorielles :

$$\begin{cases} \boldsymbol{j}_s = \mathsf{L}_{ss}\,(-\nabla T) + \sum_B \mathsf{L}_{sB}\,\big(-\nabla\mu_B - q_B\,\nabla\varphi\big)\,, \\ \boldsymbol{j}_A = \mathsf{L}_{As}\,(-\nabla T) + \sum_B \mathsf{L}_{AB}\,\big(-\nabla\mu_B - q_B\,\nabla\varphi\big)\,, \quad A = 1, \ldots, r\,. \end{cases} \tag{10}$$

$$\begin{aligned} \mathsf{L}_{sA} &= \mathsf{L}_{As}\,, \qquad A = 1, \ldots, r\,, \\ \mathsf{L}_{AB} &= \mathsf{L}_{BA}\,, \qquad A,\, B = 1, \ldots, r\,. \end{aligned} \tag{11}$$

- Relation phénoménologique linéaire pour la densité de courant tensorielle :

$$\boldsymbol{\tau}^{\mathrm{fr}}_{\mathrm{d}} = \mathsf{L}\,\mathring{\overset{\approx}{\nabla}}\boldsymbol{v}\,. \tag{12}$$

Thermodynamique

And these are the phenomenological relations linear for vector current densities. Concerning the phenomenological relationship which appears in this phenomenological relation, we have this relationship of reciprocity in his station. According to this relation, it s is equal to l to s while it has b is equal to l a and finally we have the following longitudinal relationship. For the tensor current density. According to this relation, the part of the friction tensor is proportional to the diatonic part of the deformation time. Given that our environment is called satrapy, all these phenomenological coefficients are scalars. In addition, the coefficients that appear in this phenomenological relation. Is a scalar quantity and it is identified as the coefficients of viscosity and shear of the mixture.

Notes

Summary

11m 38s

We have thus arrived at the end of of this part of the thermodynamic curves. In the next presentation, we will apply the thermodynamic formalism that we have just established to study two phenomena of thermal and chemical diffusion.

Notes

Summary

12m 37s