

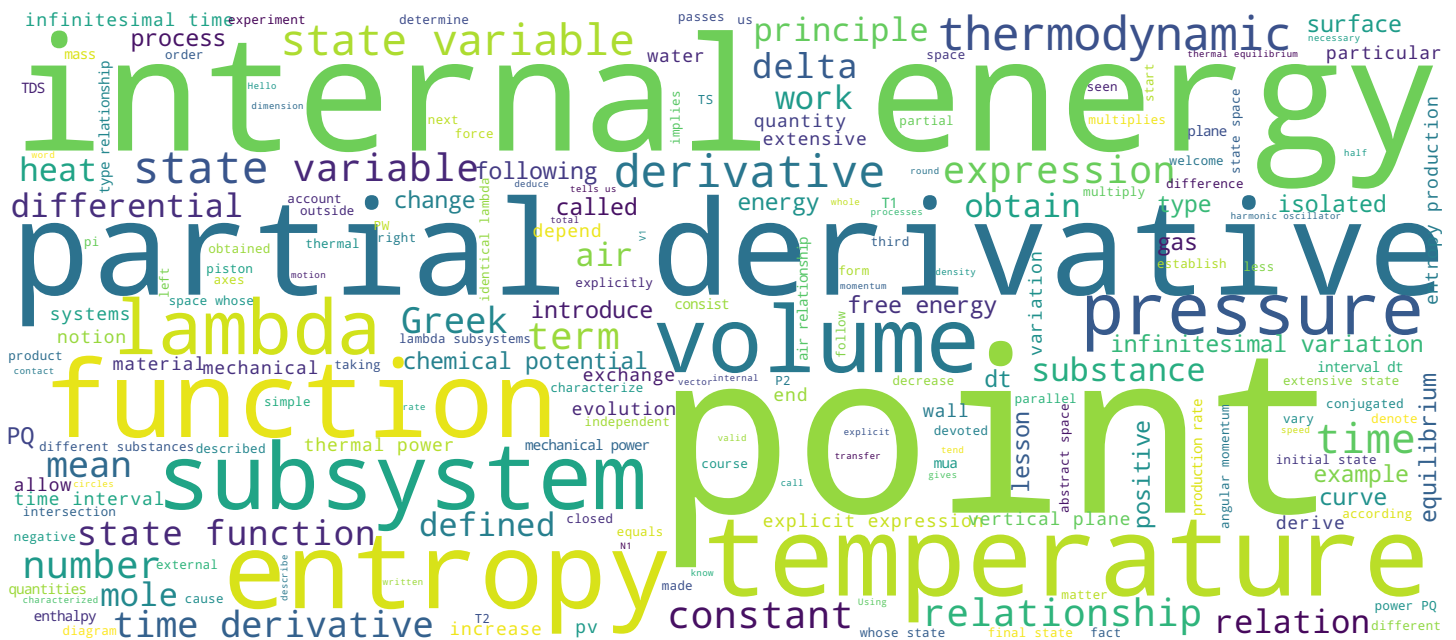
# Thermodynamique

## Relations fondamentales

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Hermann Ludwig Ferdinand von Helmholtz, 1821 - 1894



EPFL

## Video





- Relation de Gibbs
- Relation d'Euler
- Relation de Gibbs-Duhem
- Espace des états, équation d'état

Thermodynamique

Hello and welcome to make fun of thermodynamics. This lesson is devoted to the fundamental relations of thermodynamics. There are three fundamental relationships in thermodynamics. The first is the type relationship, the second is the air relationship and the third is the Duhem gypsum relationship. In this lesson we will also introduce two important concepts. These notions are the space of the States and the equation of state to derive the IPS relationship.

Notes

Summary



0m 05s

# Relation de Gibbs

- Variables d'état

- Entropie :  $S$
- Volume :  $V$
- Nombre de moles :  $\{N_A\} \quad A = 1, \dots, r$

- Dérivée temporelle de l'énergie interne :

$$\dot{U} = T\dot{S} - p\dot{V} + \sum_{A=1}^r \mu_A \dot{N}_A$$

- Identities :

$$dU = \dot{U} dt \quad \text{et} \quad dS = \dot{S} dt \quad \text{et} \quad dV = \dot{V} dt \quad \text{et} \quad dN_A = \dot{N}_A dt$$

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

Thermodynamique

- Fonctions d'état

- Energie interne :  $U(S, V, \{N_A\})$
- Température :  $T(S, V, \{N_A\})$
- Pression :  $p(S, V, \{N_A\})$
- Potentiel chimique de A :  $\mu_A(S, V, \{N_A\})$

We consider a system whose state is described by three types of state variables. First, the entropy  $S$ . Secondly, the volume  $V$  and thirdly, the number of moles of the different substances in the system. There is air substance and therefore there will be a variable number of moles for each substance and to denote the whole of these substances, well, we introduce a brace. We must also define. Certain state functions. Internal energy  $U$ . The temperature  $T$ . The pressure  $P$  and the chemical potential of the bare substance. These state functions are functions of the state variables of the system, i.e.  $S$ ,  $V$  and the set of  $N_A$ . In order to derive this type relationship. The time derivative of the internal energy is used as a basis. From the point which is equal to thirteen points minus  $PV$  points plus the sum of  $A$  also has.  $R$ . De  $\mu_A$  et  $n_A$  point. The relationship is an explicit expression of the differential of the internal energy. To obtain this expression, we will multiply the time derivative of the internal energy by the infinitesimal time interval  $dt$ , and we use the following identities.  $dU$  is equal to  $\dot{U} dt$ ,  $dS$  is equal to  $\dot{S} dt$ ,  $dV$  is equal to  $\dot{V} dt$ . For a  $dt$ ,  $dN_A$  is equal to  $\dot{N}_A dt$ .

Notes

Summary



0m 36s

# Relation de Gibbs

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- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Fonctions d'état

- Energie interne :  $U(S, V, \{N_A\})$
- Température :  $T(S, V, \{N_A\})$
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- Potentiel chimique de A :  $\mu_A(S, V, \{N_A\})$

Thermodynamique

By multiplying the expression of the time derivative of the internal energy. By the infinitesimal time interval  $dt$ , we obtain the group relation which is the following. Start. Is equal to  $TdS$ . Minus  $p dV$ , plus the sum of a  $\mu_A dN_A$ . We have thus obtained an explicit expression for the differential of the internal energy. What we would like to get now, it is an explicit relation for the internal energy.

Notes

Summary



2m 28s

# Relation d'Euler

- Extensivité de l'énergie interne ( $\lambda$  sous-systèmes identiques) :

$$U(\lambda S, \lambda V, \{\lambda N_A\}) = \lambda U(S, V, \{N_A\})$$

- Dérivée par rapport à  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} \frac{d(\lambda S)}{d\lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{d(\lambda V)}{d\lambda} + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} \frac{d(\lambda N_A)}{d\lambda} = U$$

- Variables d'état  $S, V, \{N_A\}$  indépendantes de  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} S + \frac{\partial U}{\partial(\lambda V)} V + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} N_A = U$$

- Relation d'Euler ( $\lambda = 1$ ) :

$$U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_{A=1}^r \frac{\partial U}{\partial N_A} N_A \quad \Rightarrow \quad U = T S - p V + \sum_{A=1}^r \mu_A N_A$$

Thermodynamique

Notes

This relationship is called the Euler relationship. To establish this relationship of Euler, we will use the extensibility of the internal energy of a system made of identical lambda subsystems. These subsystems are themselves simple systems. The internal energy of a simple subsystem U is a function of its entropy S, its volume V and the set of the number of moles of the different substances which constitute it and not. The total entropy of the system which consists of identical lambda subsystems. This is lambda S, the total volume, is lambda V and the number of moles of the total of the substance A. It's lambda N\_A. Therefore. Since the internal energy is a quantity extensive, the internal energy of the system U, which is a function of lambda S, lambda V and the set of lambda N\_A will be equal to lambda times the internal energy of a subsystem U which is a function of S, V and the set of N\_A. This relation can now be derived with respect to lambda. We obtain the partial derivative of U with respect to lambda S for the derivative of S with respect to lambda plus the partial derivative of U with respect to lambda V for the derivative of lambda V with respect to lambda plus the sum of R of the partial derivative of U with respect to lambda N\_A at the times the derivative of lambda N\_A with respect to lambda which is equal to U.

Summary



3m 05s

# Relation d'Euler

- Extensivité de l'énergie interne ( $\lambda$  sous-systèmes identiques) :

$$U(\lambda S, \lambda V, \{\lambda N_A\}) = \lambda U(S, V, \{N_A\})$$

- Dérivée par rapport à  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} \frac{d(\lambda S)}{d\lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{d(\lambda V)}{d\lambda} + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} \frac{d(\lambda N_A)}{d\lambda} = U$$

- Variables d'état  $S, V, \{N_A\}$  indépendantes de  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} S + \frac{\partial U}{\partial(\lambda V)} V + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} N_A = U$$

- Relation d'Euler ( $\lambda = 1$ ) :

$$U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_{A=1}^r \frac{\partial U}{\partial N_A} N_A \quad \Rightarrow \quad U = TS - pV + \sum_{A=1}^r \mu_A N_A$$

Thermodynamique

- Température :

$$T = \frac{\partial U}{\partial S}$$

- Pression :

$$p = - \frac{\partial U}{\partial V}$$

- Potentiel chimique :

$$\mu_A = \frac{\partial U}{\partial N_A}$$

The state variables of each subsystem  $S, V$  and the set of  $N$  are independent of the number of  $\lambda$  subsystems. Therefore, the derivative of  $\lambda$  with respect to  $\lambda$  is 1, the derivative of  $\lambda S$  with respect to  $\lambda$  is  $S$ , the derivative of  $\lambda V$  with respect to  $\lambda$  is  $V$  and the derivative of  $\lambda N_A$  with respect to  $\lambda$  is  $N_A$ . This reduces to the partial derivative of  $U$  with respect to  $S$ , plus the partial derivative of  $U$  with respect to  $V$ , plus the sum of one to  $R$  of the derivative partial of  $U$  with respect to  $N_A$  at a time  $N_A$  is equal to  $U$ . This relationship is independent of the explicit value of the MDA  $\lambda$ . We can take a particular value for the MDA  $\lambda$ , which means that the system consists of a single subsystem. In this particular case, this relationship reduces to  $U$  is equal to the partial derivative of  $U$  with respect to  $S$ . The more the partial derivative of  $U$  with respect to  $V$  had the more the sum of to equals one to  $R$  of the partial derivative of  $U$  with respect to one at a time one. The partial derivatives of  $U$  with respect to  $S$ . This is the temperature  $T$ . The partial derivative of  $U$  with respect to  $V$ . It's less pressure.

Notes

Summary



4m 55s



# Relation d'Euler

- Extensivité de l'énergie interne ( $\lambda$  sous-systèmes identiques) :

$$U(\lambda S, \lambda V, \{\lambda N_A\}) = \lambda U(S, V, \{N_A\})$$

- Dérivée par rapport à  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} \frac{d(\lambda S)}{d\lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{d(\lambda V)}{d\lambda} + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} \frac{d(\lambda N_A)}{d\lambda} = U$$

- Variables d'état  $S, V, \{N_A\}$  indépendantes de  $\lambda$  :

$$\frac{\partial U}{\partial(\lambda S)} S + \frac{\partial U}{\partial(\lambda V)} V + \sum_{A=1}^r \frac{\partial U}{\partial(\lambda N_A)} N_A = U$$

- Relation d'Euler ( $\lambda = 1$ ) :

$$U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_{A=1}^r \frac{\partial U}{\partial N_A} N_A \quad \Rightarrow \quad U = TS - pV + \sum_{A=1}^r \mu_A N_A$$

Thermodynamique

Notes

And the partial derivative of U with respect to at N1 is the chemical potential  $\mu_A$  of substance A. Therefore, this relationship takes the following form. It is u which is equal to TS - pV, plus the sum of  $\mu_A N_A$ . And this relationship is the relationship of the area.

Summary



# Relation de Gibbs-Duhem

- Relation d'Euler :

$$U = T S - p V + \sum_{A=1}^r \mu_A N_A$$

- Variation infinitésimale de la relation d'Euler :

$$dU = T dS + S dT - p dV - V dp + \sum_{A=1}^r (\mu_A dN_A + N_A d\mu_A)$$

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Relation de Gibbs-Duhem :

$$S dT - V dp + \sum_{A=1}^r N_A d\mu_A = 0$$

Thermodynamique

Using the type relationship and the air relationship, we are now able to derive the type relation of m. The relation of R tells us that U is equal to TS minus pv, plus the sum of a also r of mua a no. Now we have to take the infinitesimal variation of the relation of the air when taking an infinitesimal variation. We vary each term. It is necessary to differentiate this of a differential or we vary only the state variables. So the infinitesimal variation of the air relation is written d u which is equal to tds plus s dt. Minus pdv dp plus the sum of a equal to r of murder in a plus an a of the walls. It is now that we will explicitly take into account the CUPS relationship. Who says that d u is equal to TDS? Less POS? Plus the sum of. An air of loitering in. And we will subtract. The expression for the infinitesimal variation of the relationship of R. The couple relationship. And in the end, what you get, it is the relationship of the couple of the same that is next. S dt minus v dp the more the sum of a also the r of n.a will decrease equals zero. This relation of Guy Duhaime links the differentials of the quantities which are conjugated to the extensive state variables of the system.

Notes

Summary



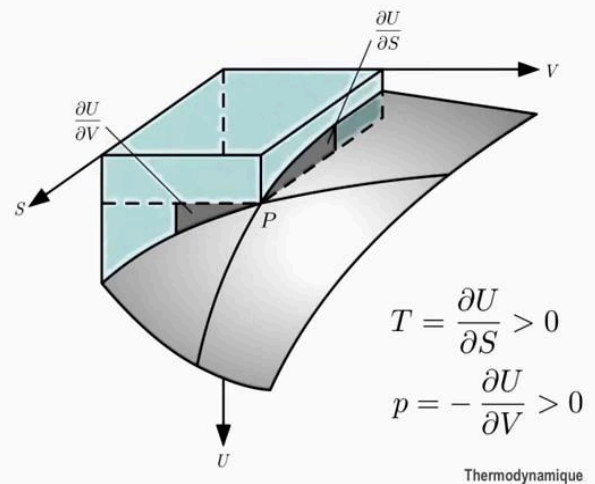
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# Espace des états, équation d'état



- Espace des états :  $\{S, U, V\}$
- Equation d'état :  $U(S, V)$  (surface grise)



Finally. We will introduce an important notion in thermodynamics, it is the space of states. the Space of States is an abstract space whose number of dimensions is equal to the number of state variables plus one. Let's take an example. Let us take a system whose state is described by the entropy  $S$  and the volume  $V$ . So we have two state variables, which means that the state space is a three dimensional space. The three axes of this abstract space are entropy  $S$ , internal energy  $U$  and volume  $V$ . the internal energy  $U$  is related to the entropy  $S$  and the volume  $V$ . By the equation of air. This equation of air is what we is called in thermodynamics an equation of state. We have a three-dimensional state space whose three axes are the entropy  $S$ , the internal energy  $U$  and the volume  $V$ . And so this equation of state. This Euler equation which gives an explicit expression of  $u$  as a function of  $s$  and  $V$ . Is a mathematical condition that will define a two-dimensional surface in the state space. This surface is the gray surface that is here. We can now represent graphically the temperature and pressure. For this, we will consider a point that lies on this space of states. It is a special state.

Notes

Summary

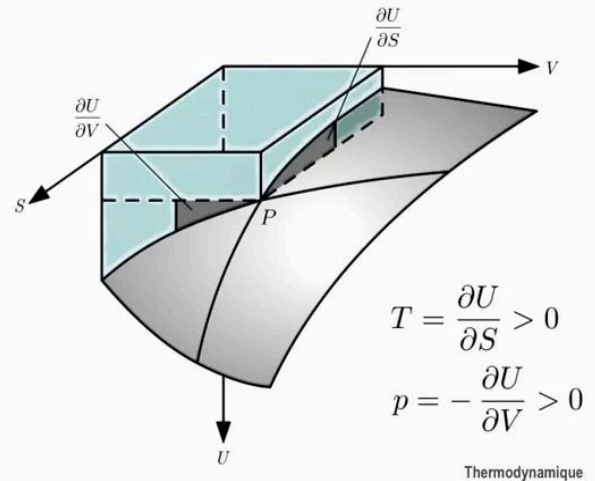


8m 51s

# Espace des états, équation d'état



- Espace des états :  $\{S, U, V\}$
- Equation d'état :  $U(S, V)$  (surface grise)



This is point P. And then we'll take a vertical plane which is parallel to the planes S and U and passes through the point P. This is the vertical plane that is here. The intersection between this vertical plane and the surface of the states in gray defines a curve in black. This curve. It is the internal energy as a function of the entropy S. With Constant. The derivative of this curve. The partial derivative of U with respect to S is the temperature. When S increases, U which directed downward increases. The temperature is defined as positive. This is exactly what this drawing shows. The pressure can now be represented graphically. The pressure is equal to minus the derivative partial internal energy of U with respect to the volume V. We take a vertical plane which is parallel to the plane U V and passing through the point P. It's this blueprint. Here, the intersection between this plane and the surface of the grey states defines a black curve that passes through point P. This curve. This EU as a function of V at constant S. The derivative of this curve. This is the partial derivative of U with respect to V. When. V increases, U decreases. Therefore, this derivative is negative, which means that the opposite of this partial derivatives of U with respect to V is equal to The pressure is defined as positive.

Notes

Summary



10m 40s