



**САМАРСКИЙ** УНИВЕРСИТЕТ  
SAMARA UNIVERSITY



# Thermodynamics of Solid State

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# Foundations of the Thermodynamics

**Subject of study:** Thermodynamics studies the phenomena caused by the action of a huge number of continuously moving molecules or other particles in the bodies that surround us.

Thermal phenomena are such changes in the system due to its atomic structure and the presence of a huge number of particles.

Thermodynamics studies thermal phenomena in matter in thermal equilibrium.

Thermodynamics is based on three experimentally established laws (principles) and does not use explicitly ideas about the structure of matter.

# Foundations of the Thermodynamics

**A macroscopic system** is any material object or body consisting of a large number of particles.

**Macroscopic parameters** are numerical values that characterize a system and its interaction with surrounding bodies (density, volume, pressure, elasticity, concentration, polarization, magnetization, etc.).

**External parameters** of the system are quantities determined by external bodies that are not part of the system (volume, external field strength, etc.).  $a_i , i = 1, 2, \dots$

**The internal parameters** of the system are quantities determined by the combined motion and distribution in space of the particles included in the system (density, pressure, energy, magnetization, etc.).  $b_i , i = 1, 2, \dots$

# Foundations of the Thermodynamics

**Internal parameters** depend, generally speaking, on the **external parameters**.

The set of independent parameters determines **the state of the system**.

A state is called **stationary** if the system parameters are time independent.

If there are no stationary flows in a stationary state, then the state is called **the state of thermodynamic equilibrium**.

**Thermodynamic system** - a system in a state of the thermodynamic equilibrium.

**Thermodynamic parameters** - these are system parameters in a state of thermodynamic equilibrium.

# The basic postulates of thermodynamics

**An isolated system** is a system that does not exchange energy, matter and radiation with surrounding bodies.

**Any isolated system in the course of time goes into a state of the thermodynamic equilibrium and cannot spontaneously go out of it.**

**Thermodynamic systems that are in a state of thermodynamic equilibrium between themselves are characterized by the same parameter - temperature.**

All thermodynamic internal parameters depend on external parameters and temperature.

$$E(T, a_1, a_2, \dots, a_n) \rightarrow T(E, a_1, a_2, \dots, a_n)$$

# Internal energy of the system. Work and Quantity of Heat

**Total energy** of system is divided into **external and internal energies**.

External energy is the energy of movement of the system as a whole and the potential energy of interaction with the field of external forces.

Internal energy is the rest of the total energy.

In thermodynamics, only internal energy is considered.

Internal energy is the internal parameter:

$$U = U(a_1, a_2, \dots, a_n, T).$$

# Internal energy of the system. Work and Quantity of Heat

There are two ways to transfer energy to a system:

- 1. The work** - a method of energy transfer associated with a change in external parameters.
- 2. Heat transfer** - a method of transferring energy to a system without changing external parameters.

The energy transferred in the first way is **the work** -  $W$

The energy transferred in the second way is **the quantity of heat** -  $Q$

# Internal energy of the system. Work and Quantity of Heat

The work  $W$  directly can change any type of energy of the system (electrical, magnetic, elastic, potential energy of the system in an external field, etc.)

The quantity of heat  $Q$  directly can change only the internal energy of the system.

At an infinitely small change in the external parameter  $a$  :

$$\delta W = A da$$

$A$  - is the conjugated to the parameter  $a$  generalized force

# Internal energy of the system. Work and Quantity of Heat

At changing several external parameters:

$$\delta W = \sum_i A_i da_i$$

## The work calculation examples.

1. Isotropic pressure:

$$\delta W = p dV \quad (A = p, a = V)$$

2. The work of a unit volume of a dielectric under the change of an electric field strength.

$$\delta W = -\frac{1}{4\pi} \left( \vec{E} d\vec{D} \right) \quad (A_i = -\frac{E_i}{4\pi}, a_i = D_i)$$

# Internal energy of the system. Work and Quantity of Heat

3. The own work of polarization:

$$\delta W_c = -E dP \quad (a = P, \quad A = -E)$$

$P$  — density of the dipol moment.

4. The work of a unit volume of a magnetic under the change of an magnetic field strength.

$$\delta W = -\frac{1}{4\pi} \left( \vec{H} d\vec{B} \right) \quad (A_i = -\frac{H_i}{4\pi}, \quad a_i = B_i)$$

$$i = 1, 2, 3.$$

# Internal energy of the system. Work and Quantity of Heat

5. The own work of magnetization:

$$\delta W_c = -H dM \quad (a = M, \quad A = -H)$$

$M$  — is density of the magnetic dipol moment.

6. The work of a unit volume of a solid at uniform deformation:

$$\delta W = \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij}$$

$\sigma_{ij}$  - is stress tensor;  $\varepsilon_{ij}$  - is strain tensor.

# Internal energy of the system. Work and Quantity of Heat

The caloric (energy) equation of state:

$$U = U(a_1, a_2, \dots, a_n, T).$$

The thermal equation of state:

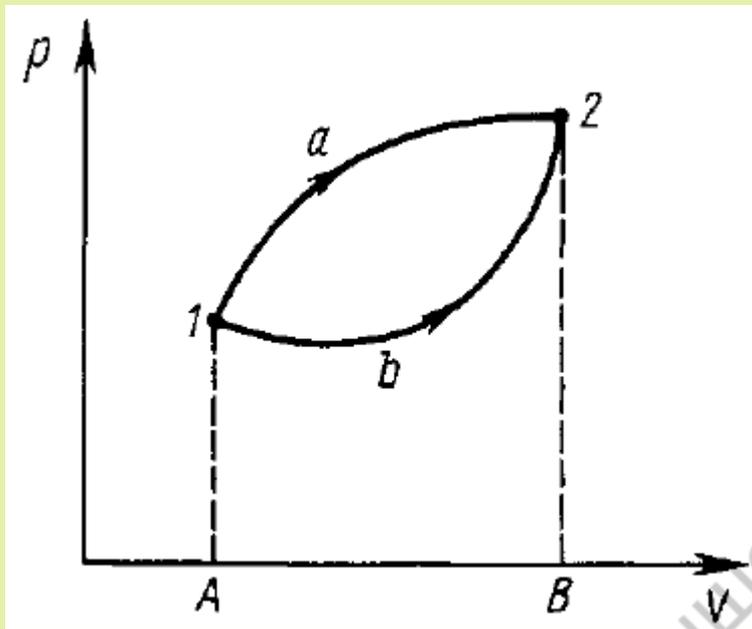
$$A = A(a_1, a_2, \dots, a_n, T)$$

In the simple systems:

$$p = p(V, T) , \quad U = U(V, T) .$$

# The first law (principle) of thermodynamics

The internal energy of the system is an unambiguous function of its state and changed only under the external influences.



$$Q = U_2 - U_1 + W .$$

$$(U_2 - U_1)_a = (U_2 - U_1)_b .$$

$$W_a \neq W_b .$$

$$Q_a \neq Q_b .$$

$$\delta Q = dU + \delta W .$$

# The first law (principle) of thermodynamics

$$\delta Q = dU + \sum_{i=1}^n A_i da_i .$$

Since the state of the system is determined by external parameters and temperature, the second law of thermodynamics can be written as the first Pfaff form:

$$\delta Q = \left( \frac{\partial U}{\partial T} \right)_{a_1, \dots, a_n} dT + \sum_i \left[ \left( \frac{\partial U}{\partial a_i} \right)_{a_k, T} + A_i \right] da_i$$

# The second law (principle) of thermodynamics

Different formulations of the second law of the thermodynamics:

## **1. The *Perpetuum Mobile* of the second kind is impossible.**

This means that it is impossible to convert heat into work without compensation, that is, without transferring part of the heat from the working body of the engine to the surrounding bodies.

## **2. The second law of thermodynamics postulates the existence in any thermodynamic system of a special function of state - entropy and its non-decrease in isolated and adiabatically isolated systems at any processes.**

# The second law (principle) of thermodynamics

3. The second law of thermodynamics is a consequence of the adiabatic unreachable principle of Carathéodory and leads to the existence of an integrating factor in the Pfaff form  $\delta Q$  .

$$\frac{\delta Q}{T} = dS$$

$S$  — is a entropy,  $T$  — is a thermodynamical (absolute) temperature.

$$\oint \frac{\delta Q}{T} = 0 . \quad \text{- is the Clausius equality}$$

# The second law (principle) of thermodynamics

## Reversible and irreversible processes

The process of transition of a system from state 1 to state 2 is called **reversible** if the return of the system to the initial state (from 2 to 1) can be carried out without changes in the surrounding bodies.

The process of transition of a system from state 1 to state 2 is called **irreversible** if the return of the system to the initial state (from 2 to 1) cannot be carried out without changes in the surrounding bodies.

# The third law (principle) of thermodynamics

At  $T \rightarrow 0$  the entropy of any equilibrium system in the isothermal processes does not depend on any thermodynamic parameters and at  $T = 0$  takes the same value for all systems.

$$\lim_{T \rightarrow 0} [S(T, x_2) - S(T, x_1)] = 0 ,$$

$x$  — is any thermodynamic parameter of the system.

# Thermodynamic potentials

1. The independent variables -  $S, V$

$$dU = TdS - pdV \quad U = U(S, V)$$

$$T = \left( \frac{\partial U}{\partial S} \right)_V, \quad p = - \left( \frac{\partial U}{\partial V} \right)_S$$

2. The independent variables -  $T, V$

$$TdS - d(TS) = dU + pdV - d(TS) .$$

$$d(U - TS) = -SdT - pdV .$$

$$F = U - TS .$$

# Thermodynamic potentials

$$dF = -SdT - pdV$$

$F$  — is the Helmholtz free energy.

$$S = - \left( \frac{\partial F}{\partial T} \right)_V, \quad p = - \left( \frac{\partial F}{\partial V} \right)_T$$

$$\left( \frac{\partial^2 F}{\partial V \partial T} \right)_{TV} = \left( \frac{\partial^2 F}{\partial T \partial V} \right)_{VT},$$

# Thermodynamic potentials

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V ,$$

$$p = - \left(\frac{\partial F}{\partial V}\right)_T = - \left(\frac{\partial U}{\partial V}\right)_T + T \left(\frac{\partial S}{\partial V}\right)_T ,$$

The energy equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p ,$$

# Thermodynamic potentials

The physical meaning of free energy  $F$  :

$$T = \text{const} , dF = -pdV .$$

3.The independent variables -  $T, p$

$$dF + d(pV) = -SdT - pdV + d(pV) ,$$

$$d(F + pV) = -SdT - Vdp .$$

$$\Phi(T, p) = F + pV = U - TS + pV .$$

$$d\Phi = -SdT + Vdp .$$

$\Phi(T, p)$  - is the Gibbs energy

# Thermodynamic potentials

4. The independent variables -  $S, p$

$$dU + d(pV) = TdS - pdV + d(pV) ,$$

$$d(U + pV) = TdS + Vdp ,$$

$H(S, p) = U + pV$  . - is the enthalpy

$$dH = TdS + Vdp .$$

The physical meaning of the enthalpy.

$$p = \text{const} , dH = TdS = (\delta Q)_p .$$

# Thermodynamic potentials

1. The general relations:

$$X = X(W) , Y = Y(W) , Z = Z(W) .$$

- three thermodynamic variables.

$$\left( \frac{\partial X}{\partial Y} \right)_Z = \frac{1}{\left( \frac{\partial Y}{\partial X} \right)_Z} .$$

$$\left( \frac{\partial X}{\partial Y} \right)_Z = - \left( \frac{\partial Y}{\partial Z} \right)_Y \left( \frac{\partial Z}{\partial Y} \right)_X .$$

$$\left( \frac{\partial X}{\partial Y} \right)_Z = \left( \frac{\partial X}{\partial W} \right)_Z \left( \frac{\partial W}{\partial Y} \right)_Z$$

# Thermodynamic functions and relations between them

The heat capacity:

$$C = \frac{\delta Q}{dT} = T \frac{dS}{dT} .$$

The heat capacity at constant pressure:

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

The heat capacity at constant volume:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

# Thermodynamic functions and relations between them

The adiabatic compressibility:

$$k_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S$$

The isothermal compressibility :

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

The corresponding bulk modulus:

$$B_S = \frac{1}{k_S}, \quad B_T = \frac{1}{k_T}.$$

# Thermodynamic functions and relations between them

The thermal expansion coefficient (expansivity):

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p .$$

The quantity  $\beta B_T$ :

$$\beta B_T = - \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial p}{\partial V} \right)_V = \left( \frac{\partial p}{\partial T} \right)_V$$

The Gruneisen parameter:

$$\gamma = \frac{V \beta B_T}{C_V} = \frac{V \beta B_S}{C_p} .$$

# Thermodynamic functions and relations between them

The physical meaning of the Gruneisen parameter:

$$\gamma = V \left( \frac{\partial p}{\partial U} \right)_V .$$

The some other relations:

$$C_p - C_V = T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p .$$

$$C_p - C_V = \frac{TV\beta^2}{k_T} .$$

# Thermodynamic functions and relations between them

The some other relations:

$$\kappa_T - \kappa_S = \frac{TV\beta^2}{C_p} .$$

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} = \frac{B_S}{B_T} .$$

# Condition of the thermodynamic stability

$$d^2U > 0 .$$

The homogeneous quadratic form in the variables  $dS$ ,  $dV$

$$d^2U = \left( \frac{\partial^2 U}{\partial S^2} \right)_V (dS)^2 + 2 \left( \frac{\partial^2 U}{\partial S \partial V} \right)_{VS} dS dV + \left( \frac{\partial^2 U}{\partial V^2} \right)_S (dV)^2 .$$

# Condition of the thermodynamic stability

The matrix of the coefficients of the homogeneous quadratic form must be positive definite:

$$\begin{pmatrix} a & c \\ c & b \end{pmatrix} \cdot \quad a = \left( \frac{\partial^2 U}{\partial S^2} \right)_V \quad \cdot \quad b = \left( \frac{\partial^2 U}{\partial V^2} \right)_S \quad \cdot$$

$$c = \left( \frac{\partial^2 U}{\partial S \partial V} \right)_{VS} \quad \cdot$$

$$\mu_1 + \mu_2 = a + b > 0 \quad \cdot$$

$$\mu_1 \mu_2 = ab - c^2 > 0 \quad \cdot$$

# Condition of the thermodynamic stability

The thermodynamic stability conditions:

$$C_p > C_V > 0 .$$

$$\kappa_T > \kappa_S > 0 .$$

# The anisotropic stresses and strains

$\vec{X}$  — is position of a small element in the initial configuration;

$\vec{x}$  — is position of a small element in the final configuration.

$$x_i = \sum_{j=1}^3 \alpha_{ij} X_j .$$

$$u_i = x_i - X_i$$

-is the displacement in the strain from  $\vec{X}$  to  $\vec{x}$

$$u_{ij} = \left( \frac{\partial u_i}{\partial X_j} \right) .$$

# The anisotropic stresses and strains

The distance between any two elements of mass in crystal:

$$\sum x_i^2 = \sum X_j^2 + 2 \sum \eta_{ij} X_i X_j .$$

$$\eta_{ij} = \frac{1}{2} \left( u_{ij} + u_{ji} + \sum_k u_{ki} u_{kj} \right)$$

-are the Lagrangian strain parameters.

# The anisotropic stresses and strains

The  $i$ -component of force on the surface of element:

$$f_i = \sum_j \tau_{ij} dS_j .$$

$\tau_{ij}$  -is the stress tensor.

The work done by the element against the stress:

$$\delta W = -V \sum_{ij} \tau_{ij} d\eta_{ij} .$$

Comparison with the isotropic case:  $\delta W = p dV$

# The anisotropic stresses and strains

The internal energy:

$$dU = TdS + V \sum_{ij} \tau_{ij} d\eta_{ij} .$$

The Helmholtz free energy:

$$dF = -SdT + V \sum_{ij} \tau_{ij} d\eta_{ij} .$$

Comparison with the isotropic case:

$$dU = TdS - pdV$$

$$dF = -SdT - pdV$$

# The anisotropic stresses and strains

Due to rotational invariance, there is a dependences:

$$U(\vec{x}, T) = U(\vec{X}, \eta_{ij}, S)$$

$$F(\vec{x}, T) = F(\vec{X}, \eta_{ij}, T)$$

Comparison with the isotropic case:

$$U = U(V, S) , \quad F = F(V, T)$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

$$\tau_{ij} = \frac{1}{V} \left( \frac{\partial F}{\partial \eta_{ij}} \right)_{T, \eta'}$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_{\eta} .$$

Comparison with the isotropic case:

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V} , \quad p = - \left( \frac{\partial F}{\partial V} \right)_{T}$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

$$B_{ijkl}^S = - \left( \frac{\partial \tau_{ij}}{\partial \eta_{kl}} \right)_{S\eta'}$$

$$B_{ijkl}^T = - \left( \frac{\partial \tau_{ij}}{\partial \eta_{kl}} \right)_{T\eta'}$$

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S$$

Comparison with the isotropic case:

$$B_S = \frac{1}{\kappa_S}, \quad B_T = \frac{1}{\kappa_T}$$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

$$S_{ijkl}^S = - \left( \frac{\partial \eta_{ij}}{\partial \tau_{kl}} \right)_{S\tau'}$$

$$k_S = \sum_{ij} S_{iijj}^S$$

$$S_{ijkl}^T = - \left( \frac{\partial \eta_{ij}}{\partial \tau_{kl}} \right)_{T\tau'}$$

$$k_T = \sum_{ij} S_{iijj}^T$$

Comparison with the isotropic case (compressibilities) :

$$k_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S$$

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

The symmetric thermal strain tensor:

$$\beta_{ij} = \left( \frac{\partial \eta_{ij}}{\partial T} \right)_{\tau}$$

The symmetric thermal stress tensor:

$$b_{ij} = \left( \frac{\partial \tau_{ij}}{\partial T} \right)_{\eta} .$$

Comparison with the isotropic case (expansivity) :

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \cdot \beta B_T = \left( \frac{\partial p}{\partial T} \right)_V$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

The heat capacity at constant configuration:

$$C_{\eta} = T \left( \frac{\partial S}{\partial T} \right)_{\eta} = \left( \frac{\partial U}{\partial T} \right)_{\eta} .$$

The heat capacity at constant stress:

$$C_{\tau} = T \left( \frac{\partial S}{\partial T} \right)_{\tau} .$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

$$B_{ijkl}^S - B_{ijkl}^T = - \left( \frac{TV}{C_\eta} \right) b_{ij} b_{kl} .$$

$$C_\tau - C_\eta = TV \sum_{ijkl} B_{ijkl}^T \beta_{ij} \beta_{kl} .$$

Comparison with the isotropic case:

$$k_T - k_S = \frac{TV \beta^2}{C_p} . \quad C_p - C_V = \frac{TV \beta^2}{k_T} .$$

# The anisotropic stresses and strains. Thermodynamic functions and relations between them

$$\frac{C_{\tau}}{C_{\eta}} = \frac{\sum_{ijkl} B_{ijkl}^S \beta_{kl}}{\sum_{ijkl} B_{ijkl}^T \beta_{kl}} .$$

Comparison with the isotropic case:

$$\frac{C_p}{C_V} = \frac{k_T}{k_S} = \frac{B_S}{B_T} .$$

# The anisotropic stresses and strains. Condition of the thermodynamic stability.

$$d^2U_S > 0 .$$

$$d^2U_S = \frac{1}{2}V \sum_{ijkl} C_{ijkl}^S d\eta_{ij} d\eta_{kl} .$$

The Voigt notation:

$ij =$	11	22	33	32(23)	31(13)	21(12)
$\alpha =$	1	2	3	4	5	6

# The anisotropic stresses and strains.

## Condition of the thermodynamic stability.

The matrix of the coefficients of the homogeneous quadratic form must be positive definite (cubic crystal):

$$\{C_{\alpha\beta}\} = \begin{pmatrix} \hat{C}_t & \hat{0} \\ \hat{0} & \hat{C}_d \end{pmatrix} .$$

$$\hat{C}_t = \begin{pmatrix} C_{11} & C_{12} & C_{12} \\ C_{12} & C_{11} & C_{12} \\ C_{12} & C_{12} & C_{11} \end{pmatrix} .$$

# The anisotropic stresses and strains.

## Condition of the thermodynamic stability.

The matrix of the coefficients of the homogeneous quadratic form must be positive definite (cubic crystal):

$$\hat{C}_d = \begin{pmatrix} C_{44} & 0 & 0 \\ 0 & C_{44} & 0 \\ 0 & 0 & C_{44} \end{pmatrix} .$$

$$\mu_1 = C_{11} + 2C_{12} . \quad \mu_2 = \mu_3 = C_{11} - C_{12}$$

$$\mu_4 = \mu_5 = \mu_6 = C_{44} .$$

# The anisotropic stresses and strains. Condition of the thermodynamic stability.

The matrix of the coefficients of the homogeneous quadratic form must be positive definite (cubic crystal):

$$C_{11} + 2C_{12} > 0 .$$

$$C_{11} - C_{12} > 0 .$$

$$C_{44} > 0 .$$

I.P.Bazarov, Thermodynamics, M.: Lan', 2010, 344 c.  
D.C.Wallace, Thermodynamics of Crystals,  
John Wiley & Son, N.Y. 484 p.

**Thanks for attention !**