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STATISTICAL PHYSICS  
LECTURE NOTES

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# Lecture Notes 1

## 1. Overview of Thermodynamics

The first law, the energy conservation law, states that a change in the energy of the system equals the sum of the heat added to the system, the work done on the system and the chemical work done on the system:  $\Delta U = Q + W + W_C$  Its differential form is:

$$dU = TdS - pdV + \mu dN \quad (1)$$

The heat capacities measure the heat needed to raise temperature by 1K.

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p \quad (2)$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad (3)$$

The compressibility measures the fractional change in volume when we decrease pressure by one unit.

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (3)$$

$$k_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S \quad (4)$$

The thermal expansion measures the fractional change in volume when we raise isobarically the temperature by 1K.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (5)$$

The second law states that when a constrained is released the system evolves to a state of maximum entropy consistent with remaining constraints. The first consequence of the maximization of entropy is: in equilibrium the intensive variables, temperature, pressure, chemical potential, are uniform. Mathematically this is the result of setting the first derivative of entropy equal to zero.

The second consequence of the maximization process is that at equilibrium second derivatives of entropy are negative. This results in convexity properties of thermodynamic potentials. This is called thermodynamics stability. The entropy  $S$  is concave function of  $U, V, N$ . The energy  $U(S, V, N)$  is convex function. The Helmholtz free energy  $F(T, V, N)$  is concave function of  $T$  and is convex function  $V$  and  $N$ . The enthalpy  $H(S, p, N)$  is concave function of  $p$  and convex

function of S, N. The Gibbs potential  $G(T, p, N)$  is concave function of T and p and convex of N.

Here are some consequences.

$$0 \geq \left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = \left(\frac{\partial \left(\frac{1}{T}\right)}{\partial U}\right)_{V,N} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{T^2 C_V} \quad (6)$$

Hence the isochoric heat capacity is positive.

$$0 \leq \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} = -\left(\frac{\partial p}{\partial V}\right)_{S,N} = \frac{1}{V k_S} \quad (7)$$

Hence the adiabatic compressibility is positive.

$$0 \geq \left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = -\left(\frac{\partial S}{\partial T}\right)_{p,N} = -\frac{C_p}{T} \quad (8)$$

Hence the isobaric heat capacity is positive.

We have proved the following thermodynamic identities:

$$C_p = C_v + \alpha^2 VT/k_T \quad (9)$$

$$k_T = k_S + \alpha^2 VT/C_p \quad (10)$$

Since  $C_p \geq 0$  and  $k_S \geq 0$  it follows, from Eq. (10), that the isothermal compressibility is positive:  $k_T \geq 0$ . Furthermore, from Eqs. (9), (10), we find:

$$C_p \geq C_v \geq 0 \quad (11)$$

$$k_T \geq k_S \geq 0 \quad (12)$$

$$|\alpha| \leq \sqrt{\frac{k_T C_p}{VT}} \quad (13)$$

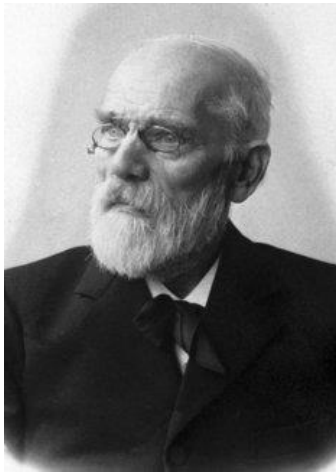
The third law (Nernst postulate) states that at absolute zero the entropy is zero:

$$T = 0; S = 0 \quad (14)$$

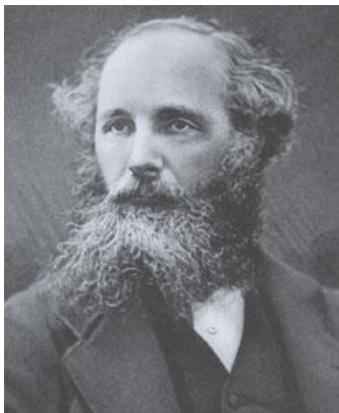
The validity of this law is connected to quantum mechanics. Intrinsic quantum systems, such as the electromagnetic radiation, satisfy it.

## 2. Phase Transitions

Water under atmospheric pressure at 0°C undergoes a transition from a solid phase (ice) to a liquid phase. At 100°C and under atmospheric pressure water boils transitioning from the liquid phase to the gas phase. The classical explanation of a phase transition involves a violation of thermodynamic stability. We will study this topic by using the van der Waals equation of state and the Maxwell construction



*Figure 1: Jaohannes Diderik van der Waals (1837-1923) Dutch physicist*



*Figure 2: James Clerk Maxwell (1831 – 1879), Scottish physicist.*

The van der Waals equation of state is:

$$(p + a/v^2)(v - b) = RT \quad (1)$$

The constants  $a$  and  $b$  depend on which chemical we study. The values for water are:

$a = 0.544 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$  and  $b = 30.5 \cdot 10^{-6} \text{ m}^3/\text{mol}$ .

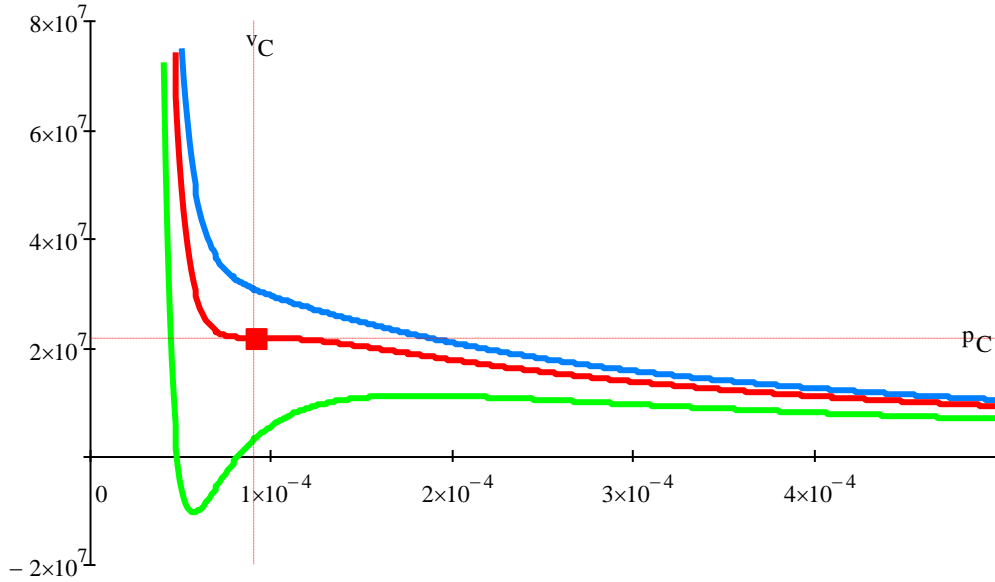


Figure 3: Water isotherms. Blue  $T = 700\text{K}$ , Green  $T = 500\text{K}$ , Red  $T = 635.646\text{K}$  (critical isotherm). Red symbol critical point  $p_C = 216.6 \cdot 10^5 \text{Pa}$ ,  $v_C = 0.0915 \cdot 10^{-3} \text{m}^3/\text{mole}$ . Pressure in Pa is on y axis; Molar volume in  $\text{m}^3/\text{mole}$  is on x axis.

High temperature isotherms, blue line in Figure 3, exhibit a monotonically decreasing pressure vs volume. This is what one expects. It is needed for thermodynamic stability: the isothermal compressibility is positive.  $k_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T > 0$ . However, on the low temperature isotherm (green line) the dependence is not monotonic. The system is unstable for a particular segment where the compressibility is negative. Maxwell interpreted this as the system separates in two phases, liquid and gas. The Maxwell construction is a horizontal segment chosen so that the two areas between the horizontal line and the  $p(v)$  curve are equal. This is equivalent to the equality of the chemical potential in the liquid and gas phases. Indeed, since  $d\mu = -sdT + vdp$ , the equality of chemical potentials  $\mu_L = \mu_G$  implies  $\int v dp = 0$ , or:

$$0 = \int_{v_L}^{v_G} v \frac{dp}{dv} dv = \int_{v_L}^{v_G} \left[ \frac{dpv}{dv} - p \right] dv = \hat{p} (v_G - v_L) - \int_{v_L}^{v_G} p dv .$$

The first term is area of rectangle under  $p^{\text{hat}}$  between  $v_G$  and  $v_L$  and the second term is the area under the  $p(v)$  curve between  $v_G$  and  $v_L$ . Thus, in Figure 4, the area I and area II are equal.

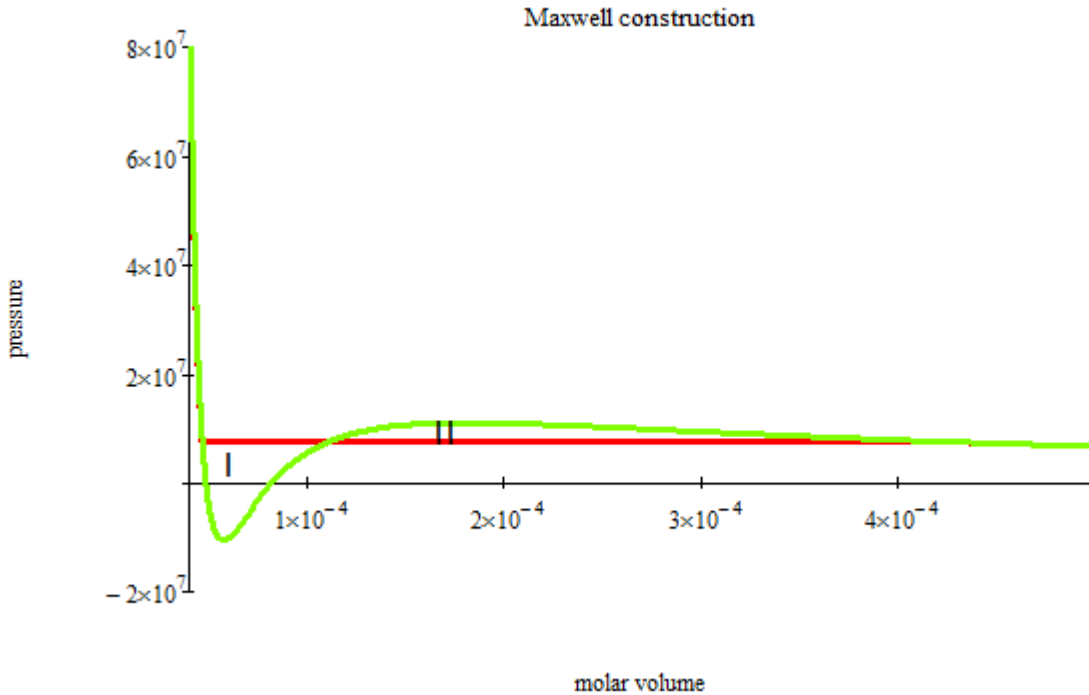


Figure 4: Maxwell construction: areas I and II are equal.

In between the high and low temperature isotherms is the critical isotherm, red line in Figure 3.

The critical point is an inflexion point:

$$0 = \frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \quad (2)$$

$$0 = \frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \quad (3)$$

We solve Eqs (2) and (3) for temperature and volume. Then we substitute those values in the equation of state Eq (1) to calculate the pressure. We find:

$$v_C = 3b; RT_C = 8a/(27b); p_C = a/(27b^2). \quad (4)$$

In view of Eq. (2), at the critical point the isothermal compressibility is infinite:  $k_T = \infty$ .

We can rewrite the equation of state (1) by using dimensionless pressure, volume and

temperature:  $p^* = p/p_C$ ;  $v^* = v/v_C$ ;  $T^* = T/T_C$ . We find:

$$(p^* + 3/v^{*2})(3v^* - 1) = 8T^* \quad (5)$$

Equation (5) expresses the law of corresponding states. The equation of state (5) written with the scaled quantities is universal, independent of chemistry.

Exercise: Calculate the critical point coordinates for water.

$a = 0.544 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$  and  $b = 30.5 \cdot 10^{-6} \text{ m}^3/\text{mol}$ . We find by substituting  $a$ ,  $b$  in Eqs. (4):

$v_C = 9.15 \cdot 10^{-5} \text{ m}^3/\text{mole}$ ;  $p_C = 216.6 \cdot 10^5 \text{ Pa}$ ;  $T_C = 635.646 \text{ K}$ .

We calculate the isothermal compressibility  $k_T$  from  $p = 8T/(3v-1) - 3/v^2$

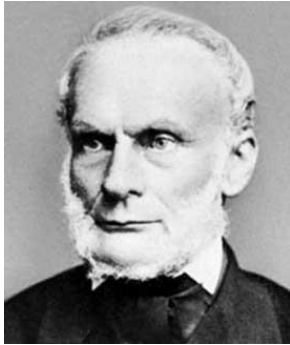
$$k_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = \frac{-1}{v \left( \frac{\partial p}{\partial v} \right)_T} = \frac{1}{6 \left( \frac{4T}{(3v-1)^2} - \frac{1}{v^2} \right)} \quad (6)$$

We calculate the thermal expansion  $\alpha$  from:  $T = (1/8)(p + 3/v^2)(3v-1)$ .

$$\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{1}{v \left( \frac{\partial T}{\partial v} \right)_p} = \frac{8}{3 \left( \frac{8T}{3v-1} - \frac{6}{v} + \frac{2}{v^2} \right)} \quad (7)$$

Note at the critical point,  $v = T = 1$ , Eqs. (6) and (7) give infinite compressibility and thermal expansion:  $k_T = \alpha = \infty$ .

### 3. Clausius-Clapeyron Equation



*Figure 5: Rudolf Clausius (1822 – 1888), German physicist*



*Figure 6: Benoit Clapeyron (1799-1864), French physicist*

The Clapeyron equation relates the slope of the coexistence curve  $p = p(T)$  to the jumps in entropy and density at the coexistence line. For sake of being explicit, we will assume the two coexisting phases are a liquid and a gas phase. The second law, entropy maximization, implies the equality of the intensive variables in the coexisting phases:

$$\mu_G(p,T) = \mu_L(p,T) \quad (8)$$

Equation (8) determines the coexistence curve  $p = p(T)$ . Then we differentiate (8) with respect to  $T$ :

$$\left(\frac{\partial \mu_G}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial \mu_G}{\partial T}\right)_p = \left(\frac{\partial \mu_L}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial \mu_L}{\partial T}\right)_p \quad (9)$$

But the differential of the chemical potential, using the Gibbs-Duhem equation, is:

$d\mu = -sdT + vdp$ . Hence equation (9) becomes:

$$v_G \frac{dp}{dT} - s_G = v_L \frac{dp}{dT} - s_L \quad (10)$$

Solving equation (10), we get the slope  $dp/dT$ :

$$\frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} \quad (11)$$

One defines the latent heat:  $l = T(s_G - s_L)$ . This heat is needed to be delivered to the liquid to boil into the gas, at fixed pressure and temperature.

$$\frac{dp}{dT} = \frac{l}{T(v_G - v_L)} \quad (12)$$

Equation (12) is the Clapeyron equation. A useful approximation of the Clapeyron equation, due to Clausius, is valid far from the critical point where  $v_G \gg v_L$  and the gas can be treated as an ideal gas:  $v_G = RT/p$ . Equation (12) becomes:

$$\frac{dp}{dT} \cong \frac{l}{Tv_G} \cong \frac{lp}{RT^2} \quad (13)$$

Application: Compute the slope of the coexistence curve  $dp/dT$  for water in the following cases:

- (a) boiling under atmospheric pressure  $T = 100^\circ\text{C}$ , latent heat  $l = 540\text{cal/g}$ ,  $v_G = 1.6729\text{l/g}$ ,  $v_L = 1.044 \cdot 10^{-3}\text{l/g}$ ; (b) freezing under atmospheric pressure  $T = 0^\circ\text{C}$ , latent heat  $l = 80\text{cal/g}$ ,  $v_S = 1.25\text{cm}^3/\text{g}$ ;  $v_L = 1.0\text{cm}^3/\text{g}$ .

We use Eq. (12).

(a)  $dp/dT = (540 \cdot 4.184 \cdot 1000) / [373 \cdot (1.6729 - 0.001044)] = 3.6 \cdot 10^3 \text{Pa/K}$ .

(b)  $dp/dT = (80 \cdot 4.184 \cdot 1000) / [273 \cdot (0.001 - 0.00125)] = -4.9 \cdot 10^6 \text{Pa/K}$ .

Note the slope of the melting line is negative and it is, in magnitude, much larger than the slope of the boiling line.

#### 4. Gibbs Phase Rule

Here is generic phase diagram of a pure chemical substance. It includes the coexistence lines for liquid-gas (boiling), solid-liquid (melting) and solid-gas (sublimation). The intersection of the three coexistence line is the triple point. For water it occurs at  $p = 0.00611 \cdot 10^5 \text{Pa}$ ,  $T = 273.16\text{K}$ .



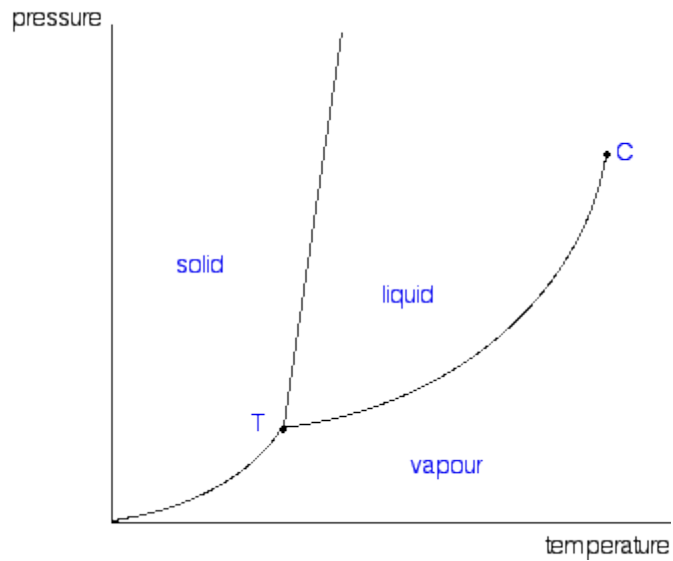


Figure 7: Generic phase diagram

At the triple point the chemical potentials of the 3 phases are equal:  $\mu_s(T,p) = \mu_l(T,p) = \mu_g(T,p)$ .

Those are 2 equations with 2 un-knowns: T and p, the triple point coordinates.

Gibbs has generalized this to a mixture of c chemicals and coexisting in r phases. The fundamental equation  $\mu_c = \mu_c(T, p, \mu_1, \dots, \mu_{c-1})$  The equality of the r values of the chemical potential  $\mu_c, \mu_c^{(1)} = \mu_c^{(2)} = \dots = \mu_c^{(r)}$ , results in r - 1 equations with c + 1 un-knowns. To have a solution the number of equations should be smaller or equal to the number of un-knowns:

$r - 1 \leq c + 1$  or  $r \leq c + 2$ . This is the Gibbs phase rule. For a pure substance c = 1 and thus  $r \leq 3$ .

### Reading

Callen Ch. 12;  
Problem Set 1.

## Lecture Notes 2

### 1. Statistical Mechanics: Microcanonical Ensemble

Consider an insulated system. A macrostate is determined by the energy  $U$ , the number of particles  $N$  and the volume  $V$ . Corresponding to this macrostate there are  $\Omega$  microstates or quantum states. The first postulate states that all microstates are equally probable. The second postulate, due to Boltzmann, states that the entropy  $S$  associated with the macrostate is:

$$S = k_B \ln(\Omega) \quad (1)$$



*Figure 1:* Ludwig Boltzmann (1844 – 1906) was an Austrian physicist who discovered the statistical interpretation of the entropy and of the second law of thermodynamics. His tombstone bears the inscription of the entropy formula.

The Boltzmann constant is a fundamental constant. Its value is:  $k_B = 1.381 \cdot 10^{-23} \text{ J/T}$ .

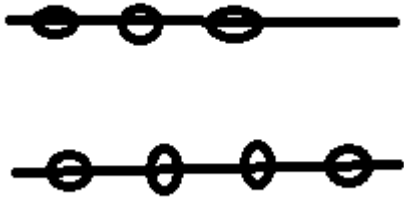
Equation (1) insures the entropy is additive. Indeed, for two subsystems with number of microstates  $\Omega_1$  and  $\Omega_2$  respectively, the total number of microstates is  $\Omega = \Omega_1 \Omega_2$ . From Boltzmann's formula one gets:  $S = S_1 + S_2$ .

During a macroscopic measurement, the system undergoes many random transitions among its microscopic (quantum) states which are assumed to be equally probable. The ergodic postulate of statistical mechanics states that the experimental time average equals the ensemble average.

## 2. Two-state system

We analyze now a system of  $N$  distinguishable particles that can occupy two energy states. The particles are distinguishable by their location. The magnetic properties of an electron gas (metal) will be discussed later in the course when we will account for the indistinguishability of the electrons. We consider of an atom that has a spin  $\frac{1}{2}$  so in the presence of an external magnetic field  $H$  its energy is either  $-\varepsilon = -\mu_B H$  or  $\varepsilon = +\mu_B H$ . The Bohr magneton is  $\mu_B = eh/(4\pi m) = 9.27 \cdot 10^{-24} \text{ J/T}$ , where  $e$  is the electron's charge and  $m$  is the electron's mass.

We have  $N$  atoms with a total energy  $U$ .  $N_+$  have each an energy  $\varepsilon$  and  $N_-$  have each an energy  $-\varepsilon$ .



*Figure 2:* Example of two-state system:  $N_+ = 3$  atoms have each energy  $\varepsilon$  and  $N_- = 4$  atoms have each energy  $-\varepsilon$ .

Hence:

$$U = N_+ \varepsilon + N_- (-\varepsilon) \quad (2)$$

$$N = N_+ + N_-$$

We solve the system of equations (2) to get:

$$N_+ = \frac{1}{2} \left( N + \frac{U}{\varepsilon} \right) \quad (3)$$

$$N_- = \frac{1}{2} \left( N - \frac{U}{\varepsilon} \right)$$

The number of microstates is given by the number of combinations of  $N_+$  atoms out of the  $N$  atoms:

$$\Omega = \frac{N!}{N_+! N_-!} \quad (4)$$

The entropy is obtained by substituting the number of microstates in the right hand side of Eq.1.

By using the Stirling approximation:  $\ln N! = N \ln N - N$ , we get:

$$S = -Nk_B \left[ \frac{N_+}{N} \ln \left( \frac{N_+}{N} \right) + \frac{N_-}{N} \ln \left( \frac{N_-}{N} \right) \right] \quad (5)$$

After substituting  $N_+$  and  $N_-$  from Eq.(3) into Eq (5) we get the fundamental equation for the two state system:  $S(U,N)$ :

$$S = -Nk_B \left[ \frac{1}{2} \left( 1 + \frac{U}{N\varepsilon} \right) \ln \left( \frac{1}{2} \left( 1 + \frac{U}{N\varepsilon} \right) \right) + \frac{1}{2} \left( 1 - \frac{U}{N\varepsilon} \right) \ln \left( \frac{1}{2} \left( 1 - \frac{U}{N\varepsilon} \right) \right) \right] \quad (6)$$

Next we denote  $s = S/N$  and  $u = U/N$ . The temperature is obtained from the first law:

$$\frac{1}{T} = \frac{\partial s}{\partial u} = -k_B \left[ \frac{1}{2\varepsilon} \ln \left( \frac{1}{2} \left( 1 + \frac{u}{\varepsilon} \right) \right) - \frac{1}{2\varepsilon} \ln \left( \frac{1}{2} \left( 1 - \frac{u}{\varepsilon} \right) \right) \right] = -\frac{k_B}{2\varepsilon} \ln \left( \frac{1 + \frac{u}{\varepsilon}}{1 - \frac{u}{\varepsilon}} \right) \quad (7)$$

Solve Eq. (7) for the atomic energy  $u$ :

$$u = -\varepsilon \frac{e^{\frac{\varepsilon}{k_B T}} - e^{-\frac{\varepsilon}{k_B T}}}{e^{\frac{\varepsilon}{k_B T}} + e^{-\frac{\varepsilon}{k_B T}}} = -\varepsilon \tanh \left( \frac{\varepsilon}{k_B T} \right) \quad (8)$$

The isochoric specific heat (per atom) is:

$$c = \frac{\partial u}{\partial T} = k_B \left( \frac{\varepsilon}{k_B T} \right)^2 \left( 1 - \left( \tanh \left( \frac{\varepsilon}{k_B T} \right) \right)^2 \right) \quad (9)$$

We show graphs of temperature,  $T\varepsilon/k_B$ , dependence of atomic energy,  $u/\varepsilon$ , and of atomic specific heat  $c/k_B$ .

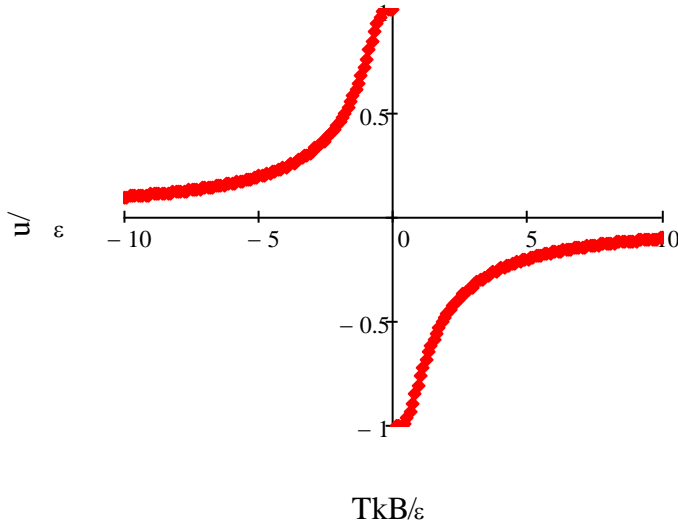


Figure 3: energy  $u/\varepsilon$  vs. temperature  $T\varepsilon/k_B$ .

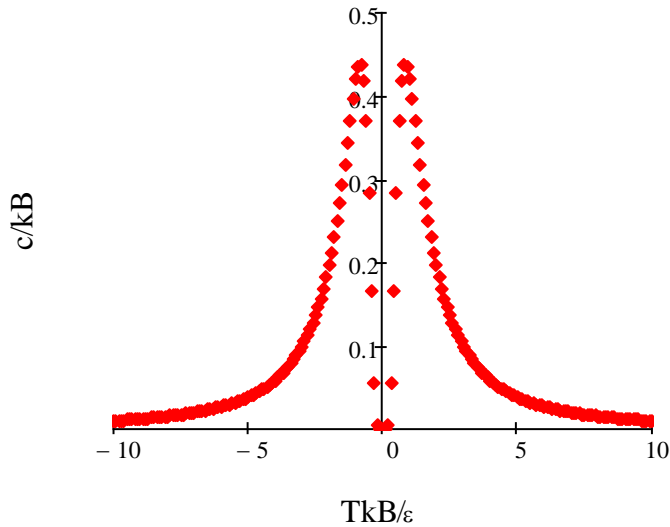


Figure 4: specific heat  $c/k_B$  vs. temperature  $T k_B / \epsilon$

Note the maximum in the specific heat, called Schottky anomaly, occurs at  $T k_B / \epsilon \approx 0.8$  and the maximum value is  $c/k_B \approx 0.44$ .

Appendix: Hyperbolic functions

$$\sinh(x) = \frac{1}{2}(e^x - e^{-x})$$

$$\cosh(x) = \frac{1}{2}(e^x + e^{-x})$$

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$\cosh(x)^2 - \sinh(x)^2 = 1$$

$$\frac{d \sinh(x)}{dx} = \cosh(x)$$

$$\frac{d \cosh(x)}{dx} = \sinh(x)$$

$$\frac{d \tanh(x)}{dx} = \frac{1}{\cosh(x)^2} = 1 - \tanh(x)^2$$

$$\frac{d \operatorname{cotanh}(x)}{dx} = \frac{-1}{\sinh(x)^2} = 1 - \operatorname{cotanh}(x)^2$$

Reading

Callen Ch. 15; Sec. 1 and 3.

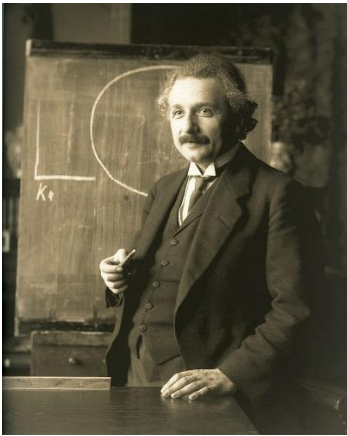
Computer lab 2.

Problem Set 2, 4.

## Lecture Notes 3

### 1. Microcanonical Ensemble: Einstein crystal

For an insulated system we use the microcanonical ensemble, consisting of copies of the system uniformly distributed among the microstates corresponding to the macrostate (U, V, N). The system transitions very fast (microscopic time scale) among the microstates (quantum) states available. According to the ergodic postulate, the time average of any system property evaluated during the (macroscopic) time of the experiment is equal to the ensemble average.



*Figure 1: Albert Einstein (1879 – 1955) theoretical physicist who discovered the theory of relativity, the photoelectric effect, the thermal properties of solids, the statistics of indistinguishable particles.*

The Einstein solid consists of N atoms or 3N independent linear harmonic oscillators. All oscillators are assumed to have the same frequency  $\omega$ . When solving the Schrodinger equation with appropriate boundary conditions, one finds the possible (quantized) values of the energy of a linear harmonic oscillator:

$$\varepsilon = (n + \frac{1}{2})\bar{h}\omega \quad (1)$$

The quantum number  $n = 0, 1, 2, \dots$ , and  $\bar{h} = h/2\pi$  where the Planck constant  $h = 6.63 \cdot 10^{-34}$ Js.

The N atoms are distinguishable by location. Their total energy is U:

$$U = \sum_{j=1}^{3N} (n_j + \frac{1}{2})\bar{h}\omega \quad (2)$$

Hence:

$$\sum_{j=1}^{3N} n_j = \frac{U - 3N\bar{h}\omega/2}{\bar{h}\omega} \quad (3)$$

In what follows I denote the energy above the zero-point energy:

$$\bar{U} = U - 3N\bar{h}\omega/2 \quad (4)$$

A microstate is defined by a sequence of  $3N$  quantum numbers:  $(n_1, n_2, n_3, \dots, n_{3N})$ . In Figure 2, we see an example of a quantum state:  $n_1 = 2, n_2 = 2, \dots, n_{3N} = 3$ .



Figure 2: Example of a microstate (quantum) state:  $3N-1$  “sticks” for the  $3N$  distinguishable linear oscillators and  $\bar{U}/\bar{h}\omega$  “marbles” for the indistinguishable quanta.

The number of microstates is given by the number of permutations of all objects (sticks and marbles)  $(3N - 1 + \frac{\bar{U}}{\bar{h}\omega})$  divided by the number of permutations of the  $(3N-1)$  identical “sticks” and by the number of permutations of the  $\frac{\bar{U}}{\bar{h}\omega}$  identical “marbles”:

$$\Omega = \frac{(3N-1 + \frac{\bar{U}}{\bar{h}\omega})!}{(3N-1)! (\frac{\bar{U}}{\bar{h}\omega})!} \quad (5)$$

The entropy is obtained by substituting the number of microstates from Eq. (5) into the right hand side of the Boltzmann entropy formula Eq.6.

$$S = k_B \ln(\Omega) \quad (6)$$

By using the Stirling approximation:  $\ln N! = N \ln N - N$ , we get:

$$S = k_B \left[ \left(3N - 1 + \frac{\bar{U}}{\bar{h}\omega}\right) \ln \left(3N - 1 + \frac{\bar{U}}{\bar{h}\omega}\right) - (3N - 1) \ln(3N - 1) - \frac{\bar{U}}{\bar{h}\omega} \ln \left(\frac{\bar{U}}{\bar{h}\omega}\right) \right] \quad (7)$$

Since  $N \gg 1$ , we approximate  $3N - 1$  by  $3N$ .

We denote atomic entropy  $s = S/N$  and atomic energy above zero-point energy  $\bar{u} = \bar{U}/N$ . It follows from equation (7) that:

$$s = k_B \left[ \left(3 + \frac{\bar{u}}{\bar{h}\omega}\right) \ln \left(3 + \frac{\bar{u}}{\bar{h}\omega}\right) - 3 \ln(3) - \frac{\bar{u}}{\bar{h}\omega} \ln \left(\frac{\bar{u}}{\bar{h}\omega}\right) \right], \quad (8)$$

where:

$$\bar{u} = u - \frac{3}{2} \bar{h}\omega \quad (9).$$

Equation (8) is the fundamental equation for the Einstein model. The temperature is obtained from the first law of thermodynamics:

$$\frac{1}{T} = \frac{\partial s}{\partial u} = \frac{k_B}{\hbar\omega} \ln\left(\frac{\bar{u}+3\hbar\omega}{\bar{u}}\right) \quad (10)$$

Solve Eq. (10) for the atomic energy above the zero point  $\bar{u}$ . Then we get u:

$$\bar{u} = \frac{3\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (11)$$

$$u = \frac{3}{2}\hbar\omega + \frac{3\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (12)$$

From Eq. (11) we get the average quantum number n is:

$$n = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (13)$$

Equation (13) represents the Bose-Einstein distribution of phonons.

The isochoric specific heat (per atom) is:

$$c = \frac{\partial u}{\partial T} = 3k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{\left(e^{\frac{\hbar\omega}{2k_B T}} - e^{-\frac{\hbar\omega}{2k_B T}}\right)^2} \quad (12)$$

The Einstein temperature is the characteristic temperature:  $T_E = \frac{\hbar\omega}{k_B}$ . We graph the atomic specific heat  $c/k_B$  vs. the temperature,  $T/T_E$ :

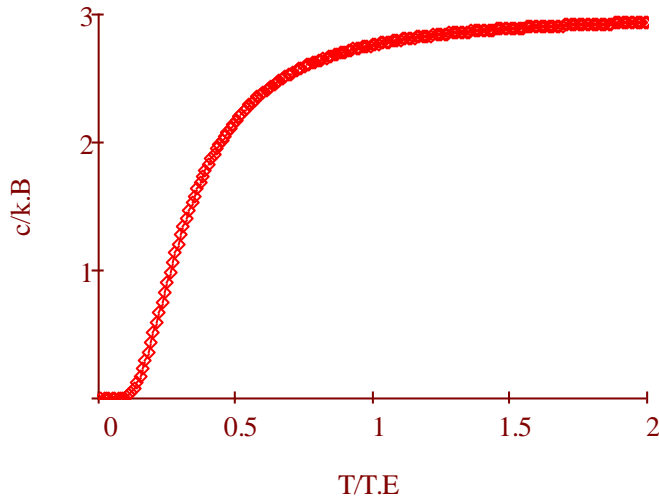


Figure 3: specific heat  $c/k_B$  vs. temperature  $T/T_E$

For  $T \ll T_E$ , the specific heat approaches zero. This is a quantum effect related to the third law of thermodynamics. Einstein's model, published in 1906, is based on the quantization of the energy. It explains this result.



For  $T \gg T_E$ , we get the Dulong - Petit law:  $c = 3k_B$ . The specific heat for 1 mole of solid is:  $c = 3R = 6\text{cal/mole}^\circ\text{C}$ . This was discovered experimentally in 1819 by Dulong and Petit who have measured specific heat of numerous solids at room temperature.



Figure 4: Pierre Louis Dulong (1785-1838), French physicist. He and Alexis Thérèse Petit (1791-1820) measured heat capacities of many solids at room temperature.

#### Readings

Callen Ch. 15; Sec. 2.

Computer lab 3.

Problem Sets 2, 3.