

**NOTES 1: DEFINITION OF THE SOLID-STATE AND A QUICK REVIEW OF THERMODYNAMICS****• Definition of a solid:**

- Collection of atoms held together by cohesive forces in which the average position of each is fixed in time

**• Every solid is a physical system:**

- Internal microscopic architecture:

Three-dimensional assembly of atoms with variable composition and morphology

- External macroscopic properties:

Mechanical, electrical, magnetic...

**• Solid-state is the science that connects the microscopic particles to the macroscopic properties**

- Aspects of materials science, physics, engineering

**• Relevance of solid state to physics:**

- Much simpler to analyze than liquids (because of fixed average position of atoms) and richer in collective phenomena than gases (because of close spacing)

- The proving ground for many fundamental concepts and laws of physics dealing with the fundamental particles (e.g., electrons), “quasiparticles”, and collective excitations.

**• Relevance to engineering:**

- Solids are the basis for most artificial (i.e., human-made) machines and electronic systems.

- Solids are strong, environmentally robust, and can generally be synthesized to have superior macroscopic properties to liquids or gases.

• As in all physical systems, internal energy  $U$  is the key metric in a solid and has a fixed value in closed systems.

• Under influence by outside forces,  $U$  is changed in two ways:

(1) Work energy done on or by the solid,  $\delta W$  (“ $\delta$ ” denotes small change; an “inexact” differential)

Note: in mechanics and electromechanics, work can always be associated with a change in “potential” energy: e.g.,  $dW = \int_1^2 F(x) \cdot dx$  for work done by a force  $F$  over a distance  $x_2 - x_1$ .

(2) Heat energy that transfers into or out of the solid,  $\delta Q$

- The randomly distributed microscopic kinetic energy associated with internal modes of the solid. Note: Because heat is just microscopic kinetic energy, it can ultimately be calculated very precisely if one knows the microscopic mechanics (classical or quantum mechanical) well enough

• Thermodynamics is the accounting formalism for  $U$ :

- Connects  $U$ ,  $Q$ , &  $W$  through 1st law (conservation of energy):

$$\delta U = \delta Q + \delta W = 0 \text{ (in any “closed” system), independent of “state” of system.}$$

- Describes the “state” of the system through a surprisingly small number of macroscopic variables, such as *temperature* and *pressure*. (Note: originally, macroscopic meant measured at the human scale; now it means, averaged over very many atoms or molecules)
- Gets amazingly simple and elegant for the special “state” called equilibrium – the state whereby the macroscopic variables are *uniform* throughout the solid or system and all of the microscopic particles and/or energy levels are equally “accessible”.
- In equilibrium “state” there are always simple relationships between the macroscopic variables, the so-called “equations of state” (e.g., recall from freshman physics or chemistry the ideal gas law:  $PV = nRT$ , where  $R$  is the universal gas constant and  $n$  is the #moles).

• At or near the equilibrium state the work and heat changes can be expressed differentially through the macroscopic variables

- $\delta W$  can be converted to a differential form by expressing in terms of specific macroscopic variables such as hydrostatic pressure and volume,  $\delta W = P dV$ , or chemical potential  $\mu$  and particle number,  $\delta W = \mu dN$ , or electric field  $E$  and polarization  $P$  vectors,  $\delta W = E \cdot dP$ , or magnetic field  $H$  and magnetization  $M$  vectors,  $\delta W = H \cdot dM$ .

- Each of the work terms occurs in “conjugate” pairs, with one of the variables being *extensive* (i.e., scales with the size of the system) and the other being *intensive* (i.e., does not scale with the size of the system). For example, P is intensive and V is extensive. Some common macroscopic variables and conjugate pairs used in solid-state are listed in the Table I below.
- Important point: dV, dN, dP, etc are “exact” differential quantities (recall from elementary calculus the difference between  $\delta X$  and  $dX$ ), so that  $\int_1^2 dV = V_2 - V_1$ . But  $\int_1^2 \delta W \neq W_2 - W_1$
- But,  $X_i dY_i$  is not necessarily an exact differential since  $X_i$  might depend on other macroscopic variables other than  $Y_i$ . [e.g.,  $\int_1^2 P \cdot dV = F_2 - F_1$  where F is the antiderivative of P with respect to V, but only if P is independent of S, and therefore T]
- It turns out that the heat can also be converted to a differential form by introducing the macroscopic quantity called entropy,  $\delta Q = T dS$ , where T is the temperature and S is related to the total number of microscopic "states" accessible to the solid,  $\delta Q = T dS$ .

Table I. Conjugate pairs of variables used to describe energy exchange in solids

Conjugate Pair	Intensive Variable	Extensive Variable	Related Susceptibility
P dV	P, hydrostatic pressure	V, volume	$(1/V_0)dV/dP$ (compressibility)
$\mu$ dN	$\mu$ , chemical potential	N, particle number	
E dP	E, electric field vector	P, polarization per unit volume	$\epsilon_{ij} = (\epsilon_0)^{-1} dP_i/dE_j$ (electric susceptibility)
H dM	H, magnetic field strength	M, magnetization per unit volume	$\mu_{ij} = \partial M_i / \partial H_j$ (magnetic susceptibility)
$\sum_{j=1}^6 e_j \pi_j$	$e_j$ , strain component	$\pi_j$ , stress component	$S_{ij} = \partial e_i / \partial \pi_j$ (compliance coefficients)
T dS	T, Temperature	S, entropy	$C = T (\partial S / \partial T)$ (heat capacity)

The are many specific forms of  $\delta Q$  that occur depending on how the fundamental particles are put in net motion by the external force or forces. When the particles are a subset of the solid as a whole, net motion means that the particles will almost always experience *friction* with respect to the remainder of the solid, so that the microscopic kinetic energy of the remainder will be increased. In the case of electrical forces, the net motion is called current *drift*, the friction is called *resistance*, and the Joule heating has the form

$$P_d = \mathbf{J} \cdot \mathbf{E}$$

where  $\mathbf{J}$  is the current density,  $\mathbf{E}$  is the electric field, and  $P_d$  is the power absorbed per unit volume.<sup>1</sup> Hence, the heat generated becomes a function of the measurement time,  $\Delta t$ :<sup>2</sup>

$$\delta Q = \int_t^{t+\Delta t} P_d \cdot dt = \int_t^{t+\Delta t} \left( \int_V \mathbf{J} \cdot \mathbf{E} \cdot dV \right) \cdot dt$$

As expressed through the current density  $\mathbf{J}$ , the drift is often linearly proportional to the external force (expressed as the electric field  $\mathbf{E}$ ) through Ohm's law which in its most general form is simply  $\mathbf{J} = \sigma \mathbf{E}$ . If  $\mathbf{J}$  and  $\mathbf{E}$  are uniform (as they tend to be in the ubiquitous circuit elements we know as *resistors*), then

$$\delta Q = \int_t^{t+\Delta t} \left( \int_V \sigma E^2 \cdot dV \right) \cdot dt$$

This expression is incredibly useful and pervasive in electrical engineering.

### Example 1. Work and heat in electrical circuits.

**Problem:** Suppose one has the elementary electrical circuit of Fig. XX in which a battery of voltage  $V_B$  is in series with an ideal switch, an ideal capacitor ( $C$ ) and a linear resistor ( $R$ ). The capacitor voltage  $V_C$  is initially zero and the switch is open; then at time  $t = 0$  the switch is turned on. What is the work performed  $\Delta W$  done by the battery, the heat generated  $\Delta Q$ , and the total energy change  $\Delta U$  in the circuit after a period  $t \gg RC$  ?

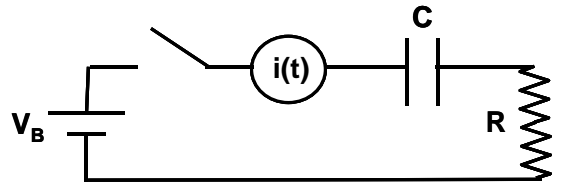
**Solution:** From the Kirchoff voltage law and at  $t > 0$ ,  $V_B + V_C + V_R = 0$ . And the series connection requires  $I_C = C(dV_C/dt) = I_R$ . The resulting differential for  $V_C$  is  $C dV_C/dt + (V_C - V_B)/R = 0$ , a linear inhomogeneous 1<sup>st</sup>-order differential equation with constant coefficients. By inspection the particular solution is  $V_C = V_B$ , and the homogeneous solution is  $V_C = A \exp(-t/RC)$  where  $A$  is a constant. So the complete solution that satisfies the initial condition  $V_C(t=0) = 0$  is just

$$V_C = V_B[1 - \exp(-t/RC)] \tag{E.1}$$

<sup>1</sup> one of the great exercises of Maxwell's equation of electromagnetics; see for example, F. Ulaby "Applied Electromagnetics," (Prentice Hall, New York, 1999), Sec. 4.7.2

<sup>2</sup> Incidentally, the time dependence in this case is a good example of why the topic is entitled *thermodynamics*, and not *thermostatics*.

The work on the capacitor is given by the change in potential energy  $\Delta U_C$  between  $t = 0$  and  $t = \infty$  associated with electric field inside,  $U_C = (1/2)C(V_C)^2$ . Because for an ideal capacitor  $C$  is independent of voltage,  $dU_C = CV_C dV_C$  is an *exact* differential, and thus  $\Delta U_C = U_C(t = \infty) - U_C(t = 0)$ , which for the solution given by E.1 becomes  $\Delta U_C = (1/2) C(V_B)^2 \equiv \Delta W$ , electrical work done by battery. To get the heat, we start with the famous Joule expression for the power dissipated by a circuit resistor,



Equivalent circuit for Example 1.

$$P_d = \delta Q / \delta t = I^2 R \quad (E.2)$$

Now in a linear resistor,  $R$  is independent of  $I$  (or  $V$ ), so that (E.2) itself represents an exact differential in  $Q$ ,  $dQ = I^2(t)R dt$ . The instantaneous current  $I(t)$  is found from  $(V_B - V_C)/R$ , which from (E.1) becomes

$$I(t) = (V_B/R) \exp(-t/RC) \quad (E.3)$$

Hence,  $\Delta Q = \int_0^\infty (dQ / dt) dt = \int_0^\infty (V_B^2 / R) \exp(-2t / RC) dt = (1/2) CV_B^2$ . So we end up with the

remarkable result that independent of the relative sizes of  $R$  and  $C$ , the work and heat produced by the battery are equal,  $\Delta W = \Delta Q$ .

A great application of this example is the power dissipation in switched RC circuits, of which CMOS logic gates are a very important example. In this case  $V_B$  becomes the “rail” voltage,  $V_{dd}$ ,  $C_G$  the gate voltage, and  $R$  the average channel resistance of the MOSFETs during the switching cycle. If the logic gate is switched repeatedly at frequency  $f_s$ , and if  $f_s \ll 1/RC$ , then the heat generated by each switching event will recur, and the total “dynamic” power dissipation will be

$$P_{dyn} \approx f_s \Delta Q = (1/2) C_G (V_{dd})^2 f_s.$$

This expression explains beautifully two facts about modern VLSI digital electronics: (1) that as the clock frequencies and associated data rate increases, the chips tend to generate more heat and necessarily run at higher temperature, and (2) the smart way to counteract the heating effect is by reduction in  $V_{dd}$  because of its quadratic dependence. Counteracting the temperatures increases with better packaging is proving difficult since Si is already being packaged on copper-alloy heat spreaders, and copper has close to the maximum possible thermal conductivity possible from common materials (single-crystal diamond is more than a factor-of-two better, but brings obvious economic problems).

- The differential form for the first law for the energy change at or near equilibrium:

$$dU = T dS + \sum_i X_i dY_i$$

- $X_i \rightarrow$  intensive parameter of  $i^{\text{th}}$  conjugate pair;  $Y_i \rightarrow$  extensive variable of  $i^{\text{th}}$  conjugate pair.
- The change in energy  $dU$  is now an *exact* differential!. Therefore, each of the intensive variables can be written as a partial derivative:  $X_i = (\partial U / \partial Y_i)_{Y_j, S}$  where the prime means all other  $Y_j$ s other than the one being differentiated. [e.g.,  $\mu = (\partial U / \partial N)_{Y_j, S}$ ]
- Similarly the temperature can be written as  $T = (\partial U / \partial S)_i|_{Y_i}$ ,

- A very useful result of the differential representation: susceptibilities

- Given the exact differential representation, very useful quantities are the susceptibilities:  $K = N(\partial Y_i / \partial X_i)$  or  $K = M(\partial X_i / \partial Y_i)$  where  $N$  and  $M$  are normalization constants to make  $K$  intensive or dimensionless, depending on the situation.
- The heat term also has a very important susceptibility called the heat capacity:  $C = T(\partial S / \partial T) \approx \delta Q / \delta T$ . This is very important in solid state because it usually scales with the density of particles or microscopic energy levels (often combined through the label “degrees of freedom”) in the solid. So the higher the heat capacity, the more ways the solid can distribute kinetic energy at the microscopic level.
- Heat capacity is also important because, representing the kinetic energy, it represents the ability of a solid to *conduct* out of the equilibrium state (much more on this later).
- A listing of some important susceptibilities is given in Table I.
- The utility of the susceptibilities stems from the fact that solid samples and systems are often affected only slightly by external forces, and so the perturbed quantity (intensive or extensive) is related to the unperturbed quantity by a small deviation:

$$Y = Y_0 + \left( \partial Y_i / \partial X_i \right)_{T} * \delta X_i$$

or  $Y_i - Y_0 = \delta Y_i = \left( \partial Y_i / \partial X_i \right)_{T} * \delta X_i$

- Another useful result of the differential representation: cross derivatives

- Very useful quantities are the *cross* derivatives:  
 $J = N(\partial Y_i / \partial X_j)$  or  $J = M(\partial X_i / \partial Y_j)$  between work conjugate pairs, or  
 $J = N(\partial Y_i / \partial T)$  or  $J = M(\partial X_i / \partial T)$  between a work variable and the temperature.

- In the case of the temperature cross-derivatives, these become very important quantities for solids in electronic devices and packages: e.g., expansivity,  $\alpha = (V^{-1})(\partial V/\partial T)|_{Y_i}$
- In the case of the work terms, these often become very interesting parameters for “mixed domain” devices in electrical engineering: e.g., the piezoelectric strain coefficient  $d_{ij} = (\partial e_i/\partial E_j)$

• Yet another useful result of the exact differential form of macroscopic variables:

**Maxwell relations**

- Given the exact differential form, there are very special relationships between cross derivatives resulting from elementary calculus: (Recall: when an dependent variable  $Z$  can be expressed in terms of two independent variables  $x$  and  $y$  by an exact differential  $dz = A(x,y)dx + B(x,y) dy$ , then we already know: (1)  $A = (\partial z/\partial x)|_y$  and  $B = (\partial z/\partial y)|_x$ . But this leads to a second great result:  $(\partial A/\partial y)|_y = (\partial B/\partial x)$  since the first is equivalent to  $(\partial^2 z/\partial x \partial y)$ , and the second is equal to  $(\partial^2 z/\partial y \partial x)$  which are identical operations since the *order* of differentiation does not matter when the functions  $A$  and  $B$  are well behaved.
- These special relationships become useful and insightful when applied to thermodynamic quantities:

Suppose it can be expressed uniquely in terms of  $T$  and  $P$  via an equation of state  $V = V(T,P)$ . Then  $dV = (\partial V/\partial T) dT + (\partial V/\partial P)dP \equiv V(\alpha dT + \kappa dP)$  where  $\alpha$  is the expansivity and  $\kappa$  is the compressibility. Now because  $dV$  is an exact differential in or near equilibrium, we have the useful (Maxwell) relation  $(\partial^2 V/\partial T \partial P) = (\partial^2 V/\partial P \partial T)$  or  $(\partial \alpha/dP) = (\partial \kappa/dT)$ . So if one knows the behavior of one quantum

• Deviations from the Equilibrium State: Linear Response Theory

- The formalism to this point requires the solid or system to be at or near thermodynamic equilibrium; i.e., a very large number of nanostates must exist and be equally probable.
- Consequence of the equilibrium state: (1) a limited number of macroscopic variables completely describe the energy, and (2) these variables are uniform throughout the solid.
- Equilibrium state is rarely achieved because: (1) boundary conditions within the system introduce a significant spatial gradient in one or more of the macroscopic variables,

and (2) external forces, even when scaled to atomic level, vary too rapidly in time for energy to be exchanged between particles of the solid.

- Good example of the spatial deviation from equilibrium: thermal gradient in practically any “dense” or high-speed electronic chip. In active region of the device, the “junction” temperature  $T_J$  will generally be much higher than the “case” temperature  $T_C$  at the bottom of the chip at the junction with the heat spreader. A second example is the (chemical)-potential gradient that occurs across any resistor under bias.
- Good example of the temporal deviation from equilibrium: Ohm’s law at ac frequencies beyond the scattering rate of the free electrons in a metal or semiconductor
  - ⇒ AC electric field accelerates the free electrons and increases their kinetic energy instantaneously, but energy is not exchanged with any other particles in the solid before the electric field changes phase. ⇒ the kinetic energy gained in one half of the cycle is lost during the other half, and there is no significant energy exchange when the Joule power density  $J \cdot E$  is averaged over time.

- **Simple Solution to Non-Equilibrium Problem: Macroscopic Linear Response**

- Strong microscopic interactions ⇒ many solids in devices and systems are operated only under weak perturbation by the external forces. And if strong effect does occur, it often occurs to only one subsystem of the solid (e.g., the conduction electrons in a semiconductor).
- Then, the response of the solid can often be analyzed using linear response theory whereby the gradient of the macroscopic variable induces a generalized *current density*  $j_X$ . The proportionality constant is called the “X”ivity. For example, the *conduction* current that flows in response to a suitably small thermal gradient is given by

$$j_T = -K (\partial T / \partial z) \quad \text{(Fick's law)}$$

where  $K$  is called the thermal *conductivity*. The *diffusion* current that flows in response to a suitably small gradient in particle number density is given by

$$j_N = -D (\partial N / \partial z)$$

where  $D$  is the *diffusivity*. And the electrical current that flows in response to a small gradient in electrostatic potential  $\Phi$  is

$$j_E = \sigma (\partial \Phi / \partial z) = \sigma E, \quad \text{(Ohm's law)}$$

- Macroscopic linear response becomes a cornerstone for a much broader field that will be fully developed in ECE215B/Materials206B called *Transport Theory*.



