Supplemental materials for "History dependence in thermodynamic properties of solids"

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1 The Gyftopoulos-Beretta approach to thermodynamics

In this section, the approach of Gyftopoulos-Beretta (GB) [Gyftopoulos (2005)] is briefly explained for readers who are not familiar with this approach. In the GB approach, the second law of thermodynamics precedes the zeroth and first laws. It begins with treating general thermodynamic situations: systems are not limited to single-component systems; no assumption of equilibrium is made. The whole of a power plant, ecosystems, even the earth are subjects of study. The essential point of the GB approach is based on the common observation that for any system, whatever complex, the change of state of the system eventually vanishes when the system is isolated from the environment: this is a native expression of the second law. The final state is unique, which is called equilibrium state. For a given system in an arbitrary state, we can adiabatically perform work ($W < 0$) on it or can extract work ($W > 0$) from it. For a water in an adiabatic container, we can perform work by, for example, stirring it. Conversely, when the water has a convection flow we can extract work from the flow by using, for example, a wheel paddle. While performing work on the system is always possible, there is a special case in which extracting work from the system is impossible. This is the case when the system is in equilibrium. Once the system reaches an equilibrium state, we cannot extract work any more without leaving any effect on the environment. This is generalization of a well-known statement of the second

law: it is impossible to obtain work merely by cooling single heat source without leaving any change on the environment. Heat source is a representative of equilibrium system, which is characterized by a single variable, namely, temperature T. Existence of T is premised on equilibrium, which is a result of the zeroth law of thermodynamics. By reverting this logical sequence, we can reach Definition 1: an equilibrium state is such a state from which no work can be obtained without leaving any effect on the environment. In this manner, we can assess whether the system is in equilibrium or not merely by inspecting the external effects. No information about the internal structure of a system is needed for the definition of equilibrium, as it should be. If the details of internal structure were required, the criterion for equilibrium would alter as our knowledge on the material is developed.

Definition 1 is subject to the restriction that the state of a system is allowed to change only within a given set of constraints. By constraints, it means any barrier prohibiting some freedom of motions, i.e., wall of a container, semi-permeable film separating chemical species, external fields, etc. For a gas in a container of volume V, the wall of the container is a constraint, which defines volume V as a TC. If an additional wall is inserted in the container, this creates two volumes V_1 and V_2. Suppose a chemical reaction $A_1+A_2 \to A_3$, and this reaction does not occur at room temperature. Then, the numbers of these chemical species, N_1, N_2, and N_3, can be taken by arbitrary amounts. What prevents three species from reaction is the energy barrier for the chemical reaction. When this constraint is removed, for example by heating, one of three variables N_i, cannot be taken as an independent variable. Missing one constraint corresponds to reducing the number of TCs by one. For solids, any kind of energy barrier which prohibits atom motion can be a constraint.

By using two terms, equilibrium and constraints, the second law is expressed as: *among all the states of a system that have a given U and are compatible with the given constraints, there exists one and only one stable equilibrium state* (Theorem 1). The existence of an equilibrium state is restated, in usual terms, as the state is developed in a manner to achieve the maximum in entropy. Theorem 1 guarantees the existence of the maximum-entropy state. But Theorem 1 states more. The existence of *only* one equilibrium state is emphasized. From this, the uniqueness of a set of TCs, $\{X_j\}$ for a given equilibrium state is guaranteed. In this manner, each equilibrium state must be uniquely specified by a set of $\{X_j\}$. This gives a unique function of $\{X_j\}$, *i.e.*, the fundamental relation for equilibrium. Impotence of

obtaining work from an equilibrium state implies that nonequilibrium states are inevitable for obtaining work. Nonequilibrium is a source of work. When two substances with high and low temperatures are contacted by removing the constraint which isolated them one another, these two substances turn to be a nonequilibrium state. This causes an irreversible change towards the final equilibrium state. Work can be obtained from the thermal flow from the high-T substance to the low-T substance. If this thermal flow is controlled by a reversible machine, the obtained amount of work is maximized. There are as many maximum-entropy states as the number of constraints. Concrete examples of the existence of variety equilibria for a solid are not given in GB and hence are given here. For silicon wafers, a number of atoms can be displaced into interstitial sites by electron irradiation. Every defect state corresponds a different equilibrium state. Different samples of a glass have different atom arrangements. Each structure of a glass sample is not spontaneously transformed to a different structure at temperatures lower than the glass-transition temperature. Hence, each structure of the glass is a stable equilibrium state. Otherwise, we could obtain work from a glass merely by cooling it.

A notable advantage of the GB approach is that entropy can be defined even for nonequilibrium states. Entropy of a state is defined by the degree how far the state is deviated from the equilibrium state in the given constraints. This degree is quantified by the maximum work that can be obtained within the given constraints. The maximum work is an observable, and hence can be determined by experiment, irrespective of states. The maximum work for an isolated system is called adiabatic availability. Available energy is an extension of adiabatic availability when the system is in contact with heat sources. They show that available energy is attributed to any arbitrary state of a system, whether it is equilibrium or nonequilibrium. Accordingly, entropy of any state of a system is determined by experiment, whose value is unique to that state. We do not need to worry about how to count microscopic states for nonequilibrium states, which has been long debated since Boltzmann gave a microscopic definition for entropy [Jaynes (1965), Lebowitz (1993)].

References

[Gyftopoulos (2005)] E. P. Gyftopoulos and G. P. Beretta, *Thermodynamics - Foundations and Applications* (Dover Pub., New York, 2005).

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2 FAQ

Q. 1 (Definition of equilibrium) *The author claims the definition of equilibrium by Definition 3, stating "It is impossible to change the stable equilibrium state of a system to any other state with its sole effect on the environment being a raise of the weight." However, it is unclear whether this definition has generality. Even at equilibrium, can we obtain work? For example, is Carnot cycle in equilibrium, because the operation is quasi-static? I leaned that quasi-static processes are in equilibrium.*

(A. 1) Definition 3 is actually the same as the second law statement. The statement is thus rigorous to this extent. We can regard it either as the definition of equilibrium, or as the second law statement provided that the definition of equilibrium was given beforehand.

This expression of the second law is seen, for example, J. K. Wark and D. E. Richards: *Thermodynamics*, 6th. ed. (McGraw-Hill, Boston, 1999) p. 294 in addition to E. P. Gyfropoulos and G. P. Beretta [49]. As the edition number indicates, Wark-Richards textbook is widely used as the undergraduate course of thermodynamics. If an error was made for such a fundamental issue, somebody must immediately point out.

In the present situation of argument, the system interacts with its surroundings only through work interaction. Suppose a positive work W is obtained from this system. Only possible way in order to retain the energy conservation is a reduction of the internal energy ΔU of the system: $\Delta U = -W < 0$, because of no heat interaction. This means that work is obtained by cooling the system. This contradicts a familiar expression (the Kelvin-Planck statement) that it is impossible to extract work merely by cooling a substance. In order to obtain W, use at least two substances of high and low temperatures is needed. Contacting high and low T substances creates a nonequilibrium situation. When an appropriate heat engine is inserted between them, a part of the heat flow can be converted to work. If the heat engine operates quasi-statically, the maximum performance is obtained.

At this point, I like to point out a confusion between *quasi-static process* and *equilibrium state*. The Carnot cycle is regarded as a quasi-static process. If a quasi-static process is regarded as being identical as an equilibrium state, we could say that work is obtained from the equilibrium state. But don't confuse *process* for *state*. The situation of contacting two systems with different temperatures is essentially a nonequilibrium state. Insertion of a

reversible heat engine between the two systems renders the process being at an infinitesimally slow rate: at each moment the whole system can be approximately regarded as equilibrium. In this way, regarding the Carnot engine as an equilibrium state is incorrect, or should be used in a restricted sense. When two substances become truly in equilibrium, the temperature difference vanishes, and work is no longer obtained.

The same holds for chemical reactions. Consider water reaction,

$$\mathrm{O_2} + 2\mathrm{H_2} \ \rightarrow 2\mathrm{H_2O}. \tag{1}$$

When there is initially no water, this reaction takes place, while the rate of reaction depends on T and P. By using an appropriate electrochemical set up, the generated heat of reaction can be converted to an electric work. However, eventually, the chemical equilibrium will be reached with equilibrium concentrations of involved chemical species. After reaching equilibrium, work can be no longer obtained. In this manner, the term equilibrium is used in the exact meaning.

Q. 2 (Extensiveness) *The author claims that atom positions are state variables. But, they are not extensive variables, and hence should not be state variables.*

(A. 2) Why not? It is our leaning from classical mechanics that

$$\Delta U = -f dx, \tag{2}$$

where f is the force acting on a particle and x is the displacement of it. Obviously, the position is an extensive variable. Today, in MD simulations of solids, it is a daily practice to calculate the free energy difference ΔF by tracing a particle's trajectory. Thermodynamic integration method establishes the following relationship,

$$\Delta F = \int \left\langle \frac{\partial V}{\partial x} \right\rangle dx \tag{3}$$

where V is the potential of the solid. See, D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed. (Academic, 2002), p. 171. This clearly indicates that the free energy of a macroscopic system is obtained by taking atom position as state variable. We can calculate the free energy change ΔF, even for the case in which one atom is displaced from the regular position to an interstitial position.

Q. 3 (Macroscopic nature of thermodynamics) *Atom positions are incompatible with the macroscopic nature of thermodynamics. The author introduces the time average of atomic positions as new thermodynamic coordinates for the thermodynamics of solids. However, these variables are unsuitable for describing thermodynamics as they are not macroscopic quantities.*

(A. 3) The view that thermodynamics treats only macroscopic quantities pervades deeply people's mind. In this paper, I demonstrate that this view does not meet the development of physics of solids state. For gases, the internal energy U of a gas is determined by T and V solely, when chemical reactions are ignored. Therefore, this view is good for the introductory-level thermodynamics. But for solids, this relationship $U = U(T, V)$ disagrees with numerous experimental results. For solids, displacement of even one atom into an interstitial site alters the energy U of it. Introducing a dislocation obviously changes U. Material researchers take it for granted that creating an interstitial atom increases U by the formation energy of the defect ΔE_f. Even though ΔE_f is a microscopic quantity, we can measure ΔE_f by a standard thermodynamic method, namely, the Arrhenius analysis on the T dependence of the interstitial concentration. The concentration c is proportional to $\exp(-\Delta E_f/kT)$. On the other hand, there is no proof that T and V are only independent state variables for solids: I scanned more than 50 textbooks of thermodynamics, but failed to find its proof. We cannot trust such statements that cannot be proven on thermodynamics grounds.

The view that thermodynamics is a macroscopic theory is the old and repeatedly claimed statement. However, can he say how small the microscopic scale is? How large does the macroscopic mean? Thermodynamics is a universal theory, which holds from atomic scale to astrophysical scale. Even in unclear matters, experimentalists found phase transitions, although they are in a microscopic scale. Our planet is a macroscopic object in the human scale and yet is microscopic in the astrophysical scale. Description of physics must be independent of the human view. Atom positions are microscopic in our scale. Experimentalists can know the atom positions of solids by X-ray diffraction method. X-ray diffraction patterns are recorded on X-ray films. The recorded files are macroscopic objects. I am not sure if one regards this measurement as microscopic observation. Is the Arrhenius analysis microscopic observation? In semiconductors, defect states reflect on the electrical conductivity, which is a macroscopic quantity. By measuring the electric properties, we can know the defect states. Note that there is

no word of macroscopic in the description of the thermodynamics principles from the zeroth to third law. Energy conservation and entropy increase hold, irrespective of the size of systems. People stick with the conventional view that the thermodynamics approach is to describe properties of a macroscopic system by only a few state variables. This is true for gases, but there is no reason to restrict to a few variables for complicated system such as solids.

In fact, the conventional view contradicts experiments on solids. Overwhelming experiments indicate the dependence of U on atom positions. As stated above, displacement of even one atom to an interstitial site alters the energy U of it. There are an infinite number of ways to deform the microstructure of a given crystal. Even if impurities are excluded, vacancies, interstitials, microvoids, dislocations, various grain structures, twin structures, various metallurgical textures, are observed if it is measured with sufficiently high resolutions. In all the cases, the energy U is altered by these details of atom arrangement. All the observations indicate that U depends on $\{\mathbf{R}_j\}$. Today, in the electronic theory, the view that U of a solid is determined by the structure Rjis taken for granted. This is the experimental fact and theoretical (DFT) fact. Fact is more important than the traditional belief.

The important factor determining state variables is the presence of the correlation between U and state variables. In gases, instantaneous atom positions have no correlation to U, and only the average quantity of density determines U. On the other hand, although instantaneous atom positions are random, the time averaged positions determine the microstructure and have a definite correlation to U. Gyftopoulos and Beretta describe in [49] "the state principle (it means FRE) is derived as a rigorous consequence of the first and second laws, not as a consequence either of difficulties related to exact calculations and lack of knowledge, or a need to describe complicated physical problems by a few gross macroscopic averages. (p. 119)". Existence of correlation presumes a definite value for a state variable. Microscopically, atoms are always changing their positions. The time averaged position is indeterminate for gases. On contrary, for solids we have a definite and unique value for the time averaged position. In this way, the invariance against time averaging operation is the essential requirement for state variables rather than ambiguous word of macroscopic.

Q. 4 (Independence of thermodynamics from statistical mechanics) *Today, it is the general understanding that statistical mechanics is more fundamental than thermodynamics*

(A. 4) From the contemporary point of view, properties of solids cannot be understood without information about the structure. This means that the U of a solid is a function of $\{\mathbf{R}_j\}$. Despite this, people often claim the macroscopic feature of thermodynamics, so that speaking atom position is almost a taboo. I suppose that, behind this belief, there is a deeply routed misunderstanding that statistical mechanics is an exact theory and thermodynamics is only approximation. This is not true. Both theories are equivalent.

Let us consider the difference in the two approaches by taking the specific heat of a solid as example. Today, from the microscopic view, we can know the specific heat of a solid from its phonon spectrum $g(u)$ (u is the phonon energy). Once its structure is known, irrespective of whether it has defects or not, it is a standard procedure to calculate a phonon spectrum. If defects are present, $g(u)$ will have different spectrum from that of the perfect crystal, but we can still calculate it. Then the partition function $Z(\beta)$ can be obtained by integrating

$$Z(\beta) = \int e^{-\beta u} g(u) du \tag{4}$$

From $Z(\beta)$, the free energy F, internal energy U and finally specific heat C as a function of T can be successively obtained. Now, we can proceed in the reversed order. By measuring the temperature dependence of $C(T)$ over the whole range of T, we can construct $F(T)$, $Z(T)$, and finally by inverting Eq. (1), we obtain

$$g(u) = \int e^{\beta u} Z(\beta) d\beta \tag{5}$$

Hence, even from purely macroscopic measurement, we can reach microscopic information. If the structure is changed by displacing one atom, this change is reflected in the phonon spectrum. In principle, it causes a change in $C(T)$ though only slight, so that we can detect the defect by the calorimetric method. We find that the relationships (4) and (5) are actually the Raplace transformation. This relationship between thermodynamics and statistical mechanics was pointed out by Mandenbrought, *et al.*,

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L. Tisza and P. M. Quay, Ann. Phys., **25**, 48 (1963).

The difference between statistical mechanics and thermodynamics is merely its interpretation. In thermodynamics, we do not know the substance of microscopic quantity $g(u)$. We can only accept it just as something that charac-

terizes the internal structure of a solid (Khinckin, *Mathematical Foundations of Quantum Statistics*: Dover Publications, 1998).

Q. 5 (Nonequilibrium characterization of glass) *The atom relaxation process at the glass transition is a very slow process. It is today's common understanding that freezing the glass state is a consequence of this slow process. If we can wait furthermore, the glass state will become a supercooled liquid state upon a wait with sufficiently long time.*

(A. 5) The stability of state is judged by comparing free energies of competing states. The conclusion that the free energy of glass is lower than that of liquid is proven in my previous paper [52]. I know that people often discuss the kinetic constraint for the glass transition. However, it is not clear what kind of energy is meant by stating "work to add a constraint". The total energy of a solid is given by the sum of the kinetic energy of the constituting atoms and the potential acting between them. In the calorimetric method, the change in the total internal energy of a glass is measured by adding/subtracting heat. There is no external work performed on the sample. Therefore, the substance of constraint must be the energy barrier, which is the part of potential. The work required to push into small areas must come from the potential energy, in a similar manner to the crystallization case. Accordingly, the free energy G calculated by the observed specific heat C_p is the true free energy. Then, we obtain that the free energy of glass $G_{(g)}$ is lower than that of liquid $G_{(l)}$: see Fig. A1 in [52]. This conclusion does not depend on material. It holds as far as C_p is positive (positive definiteness), because of the upward concavity of G. I think that the view of relative stability of supercooled liquid against the glass state was borne by relaxation experiment of glass transition by Davies and Jones: R. O. Davies, G. O. Jones, Proc. Roy. Soc. A **217** (1953) 26. They considered that the glass state undergoes a relaxation process towards the supercooled liquid state. Occurring of relaxation process itself is correct, but there is no evidence that the final state is the supercooled liquid state. This conclusion is obtained merely by extrapolating the enthalpy of the supercooled liquid. The thermodynamics principle of the upward concavity of G is more fundamental than the extrapolation. I discussed this analysis on G with several glass researchers, including Prof. Nemilov. I have never heard criticism on this point, because they kept silent about this point. Once we understand that the glass state is more stable than the supercooled liquid for $T < T_g$, we don't need to wait until the Kauzmann transition takes

place. I think that we need to reappraise the fate of glass transition from this free-energy consideration but not by extrapolation.

Recent DFT studies by our group indicate that this kinetic constraint is played by the potential energy of the glass [53,130]. The work to be performed to fix atom motions is no more than the binding energy of material. See Fig. 2 of [53] and Fig. 4 of [130]. There we see abrupt changes in the potential energy (there it is denoted by the structural energy $E_{\rm st}$) at T_g. In model potentials, calculation of the total energy is difficult, so that the change in the structural energy was not possible. In DFT, the total energy is the quantity of the primal importance, the change in the total energy can be obtained accurately. This is a big step in the glass research in that quantitative evaluation of the total energy is possible.

Q. 6 (Aging) *There is strong evidence that the glass state is a nonequilibrium state. Even after freezing in the glass state, the glass undergoes a change throughout a long-time period, which is known as aging.*

(A. 6) Aging is also a big issue. However, can you distinguish the process with infinitesimally slow rate of change from equilibrium? Everybody agrees that the gas in the container is in equilibrium. However, even in the robust gas cylinder, the gas cannot retain the high-pressure state in a long time. Eventually, gas is leaked out. Diamond will be eventually graphite, because the free energy of diamond is higher than that of graphite. The mixture of nitrogen and hydrogen gases is stable, and no reaction occurs at normal conditions. However, eventually they react to produce ammonia gas, because the free energy of the latter is lower than that of the former. Aging is relaxation and is a common property in any material. See Sec. 3.3 of this paper.