

Supplemental materials for “Nature of the order parameter of glass”

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1 The Gyftopoulos-Beretta approach to thermodynamics

In this section, the approach of Gyftopoulos-Beretta (GB) [Gyftopoulos05] is briefly explained for readers who are not familiar with this approach. However, for full understanding, the original textbook should be referred to.

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 $A_1 + A_2 \rightarrow A_3$, 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 [Jaynes65, Lebowitz83].

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 regarded as 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, [Wark99] in addition to [Gyftopoulos05]. As the edition number indicates, [Wark99] 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,



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 (Should we treat the OP of glass separately from others?) *Glass is a frozen-in nonequilibrium state of a liquid. Periodicity is absent in a liquid and absent also in a glass. No serious scientist has by this reason connected the order parameter in glasses with deviations from periodicity. Consequently, the discussion of the description of order in crystals performed in the introduction is senseless in application to glasses.*

(A. 2) It is surprising to hear this. I made many efforts to explain, in Introduction, how difficulties arise when we try to get the unified understanding the notion of order parameter for various materials. However, he neglected these difficulties merely by isolating the glass issue from other materials. He may be content with this. Instead, no development is expected. Other people are not happy. Probably, in most, students will feel dissatisfaction with this explanation. Physics is a universal theory. Such a theory that is valid only for glass is less attractive. There are other people trying to describe the glass transition in terms of order parameters in the general framework of phase transition, for example, DiMarzio and his co-workers [DiMarzio76, DiMarzio76a]. Even when we restrict the notion of order parameter within glass, however, many of fundamental problems of the glass transition have not yet been solved. There is no consensus about what the substance of the order parameters of glass. In this paper, I gave the concrete picture of the order parameters.

In spite of numerous studies on glass, the glass transition remains as an open question. The most significant problem is the nonequilibrium character of glass state. There is no satisfactory theory for describing nonequilibrium states. Almost all people believe that glass is a nonequilibrium state. But why is the glass state not an equilibrium state? Answering this question is possible only when the definition of equilibrium is known. In order to answer this question, we have to know which state variables other than T and P are required for solids. But this way of argument leads to circular argument between the definition of equilibrium and state variable, as pointed out by Bridgman [Bridgman50, Bridgman61]. No studies on the glass issue have been made by asking this fundamental question. The present study traces back this starting point. He neglects this fundamental problem and consider only in the glass matter. However, people outside the glass research cannot be satisfied because of the inconsistencies in the treatment between crystals and glasses. Recent establishments of the author's group [Shirai20, Shirai21, Shirai21a] provided successfully neat description of the glass transition and glass properties. In particular, the specific heat at the glass transition is well described in the present view, indicating that the glass transition is essentially structural transition [Shirai22, Shirai23]. He seems not to like to see the merits of these studies. It is, however, the time to consider the glass issue from the very fundament of thermodynamics.

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) I know that 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 of the defect is obtained as,

$$c(T) = c_0 \exp(-\Delta E_f/kT). \quad (2)$$

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 had not been 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 $\{\bar{\mathbf{R}}_j\}$. Today, in the electronic theory, the view that U of a solid is determined by the structure $\{\bar{\mathbf{R}}_j\}$ is 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 [Gyftopoulos05] “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 $\{\bar{\mathbf{R}}_j\}$. Despite this, people often claim the macroscopic feature of thermodynamics, so that speaking atom position in thermodynamics 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 $g(u)$, where 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 of a solid. 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

$$Z(\beta) = \int e^{-\beta u} g(u) du \quad (3)$$

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. (3), we obtain

$$g(u) = \int e^{\beta u} Z(\beta) d\beta \quad (4)$$

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, and thus we can detect the defect by the calorimetric method. We find that the relationships (3) and (4) are actually the Laplace transformation. This symmetric relationship between thermodynamics and statistical mechanics was pointed out by Mandenbrought, *et al.* [Mandelbrot62, Mandelbrot64, Tisza63].

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 characterizes the internal structure of a solid [Khinckin98].

Q. 5 (Corollary 1) *There is a significant jump in logic from the statement of the second law to corollary 1 that it requires the average positions of all the particles to defines the state of the system for a solid, including crystals.*

(A. 5) He complains insufficiency in the explanation of logical steps from the second law to corollary 1. This was explained in [Shirai18]. OK, here I explain the logical flow leading to corollary 1. It consists of the following steps.

1. By combining Definition 1 (equilibrium) and Definition 2 (constraint), we conclude that any structure of solids is in equilibrium as long as the solid retains its structure. Any defect state j is equilibrium within the timescale of the lifetime τ_j of that defect. The structure is fully specified by $\{\bar{\mathbf{R}}_j\}$. In this case, the corresponding constraint is the energy barrier ξ_j that restricts this atom in the vicinity of that position.
2. By definition 3 (state variable), the mean position of every atom $\bar{\mathbf{R}}_j$ can be a state variable. This is because instantaneous atom position $\mathbf{R}_j(t)$ has a definite mean value for the time average within τ_j . The definite value means a unique value, which is independent of the time period in which time average is taken. This meets the necessary condition for state variable.
3. The second law states that there is one and only one equilibrium state for a given set of constraints, which is the maximum entropy state within the constraints. Each equilibrium state can be uniquely specified by a full set of $\{\bar{\mathbf{R}}_j\}$ in addition to T . When one atom k is moved to another interstitial site $\mathbf{R}'_k$, the internal energy of this solid is altered, no matter how small it is. The internal energy U of this solid depends on all atom positions $\{\bar{\mathbf{R}}_j\}$. The last statement is confirmed by DFT: the total energy of a solid is uniquely determined by atom positions. The unique relationship $U = U(T, \{\bar{\mathbf{R}}_j\})$ is taken for granted in DFT community.

Q. 6 (Glass is nonequilibrium state) *The author claims that glass is in equilibrium. However, it is the today's standard understanding that glass is in nonequilibrium state. In fact, there are tremendous studies to support this view.*

(A. 6) I know this view. However, when someone says that glass is in nonequilibrium, he must know the definition of equilibrium. The answer to the question why glass is not in equilibrium could be different from people to people. Aside from minor issues, their reasonings are essentially ascribed to the observation that the glass properties have dependence on the past history through which it was obtained. This can be restated as the glass properties are not uniquely determined by two state variables T and V . It is true that the thermodynamic properties of gases are uniquely determined by two state variables T and V . However, there is no rigorous proof for solids, even though

presently chemical reactions are ignored. I scanned more than 50 thermodynamics textbooks about the definition of state variables for solids, but I couldn't find this. No matter how many studies have been accumulated, the view that only two state variables T and V are the independent state variables is merely an assumption for solids and we should not trust this as the fundamental postulation. Principles precede any model.

In fact, this assumption contradicts experimental facts. It is well known that the mechanical properties of iron steel depend on the past history of thermal treatments. By observing this, some people consider steel as nonequilibrium material and so steel is an exception for thermodynamics: see [Callen85] (Sec. 1.5). However, could you imagine how many exceptions are created in this manner? Such history dependence can be observed to some extent for all the other solids. Suppose that we measure the electrical resistivity of a silicon wafer. If this wafer is heated to melt and is cooled down to form again Si wafer. The concentrations of defects, such as vacancies, may be different from the initial state, and the obtained resistivity is different. In this way, if we measure carefully, we will find any solid has history dependence. If we consider that material simple because of history dependence, all solids should be considered nonequilibrium state. This is the crisis of thermodynamics. Nobody can explain why it is. Bridgman wrote this: "If at first we are unsuccessful in finding a set of parameters which determine an energy function, we do not rush to conclude that the laws of thermodynamics do not apply to our system, but rather suspect that we have not a complete list of parameters of state" [Bridgman61].

I did this according to the suggestion of Bridgman by writing a series of papers [Shirai18, Shirai20, Shirai21] including this paper. The answer is surprisingly simple, that is, by employing equilibrium positions of all the atom as the member of state variables, all thermodynamic properties of solids can be uniquely specified, irrespective of the previous history. For hysteresis, [Shirai24] is useful to understand the principles underlying hysteresis.

Q. 7 (Metastability of the glass state) *The paper relies on the incorrect conclusion that the free energy of a glass is lower than that of the liquid. This conclusion ignores the thermodynamic requirement that it requires work to add a constraint to the system that restricts the glass to a small region of configuration space compared to that of the liquid.*

(A. 7) The stability of thermodynamic states should be judged by comparing free energies of competing states but not by enthalpies. The conclusion that

the free energy of glass is lower than that of liquid is proven in my previous paper [Shirai20]. 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, as $E_{\text{tot}} = E_K + E_P$. In the calorimetric method, the change in the internal energy ($U = \bar{E}_{\text{tot}}$) 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 $G^{(l)}$: a real example of glycerol is seen in Fig. A1 in [Shirai20].

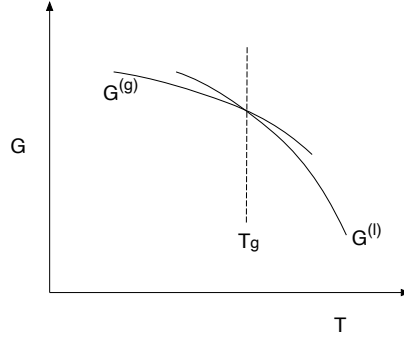


Figure 1: Free energy of glass $G^{(g)}$ and liquid $G^{(l)}$.

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 . C_p is given by the second derivative of G as

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p. \quad (5)$$

Hence, as far as $C_p^{(g)}$ and $C_p^{(l)}$ are positive, only a way of intersection of $G^{(g)}$ and $G^{(l)}$ is that shown in Fig. 1. 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 [Davies53]. 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 any 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 [Shirai22, Shirai23]. The work to be performed to fix atom motions is no more than the binding energy of material. See Fig. 2 of [Shirai22] and Fig. 4 of [Shirai23]. There we see abrupt changes in the potential energy (there it is denoted by the structural energy E_{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. 8 (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. 8) Aging is 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 [Shirai24].

Q. 9 (Redundancy in state variables) *There is some discussion regarding defects, but they seems to ignore the fact that at temperatures above absolute zero an equilibrium crystal is expected to contain an equilibrium number of defects that give rise to large set of states that all exhibit the same material properties that remain the same under different methods of preparation. This suggests that a reduced set of variables is possible as is found experimentally and in simulation. The same case can be made for glasses within the inherent structure landscape approach, although it is still generally unclear how to do this.*

(A. 9) He pointed out that there are many equilibrium configurations for a given crystal when defect states are taken into account. I am pleased to receive this question. There is no conflict with the present result. Rather, this is an important message of this paper. For solids, the internal energy U cannot be uniquely specified by T and V solely but depends on $\{\bar{\mathbf{R}}_j\}$, as $U = U(T, V, \{\bar{\mathbf{R}}_j\})$. All the existing structures of silicon with different interstitials are regarded as different equilibrium states of the same material. An interstitial atom has a different value $\bar{\mathbf{R}}_j$ from that of the regular position, and hence this state is specified by a set of $\{\bar{\mathbf{R}}_j\}$. It is my observation that many theorists ignore defect states of crystals, simply because these are metastable states. But they forget that the equilibrium concentration of defects is the direct consequence of the equilibrium condition. I am happy to hear his view.

His pointing out a reduced set of state variables is interesting. In fact, in many cases, there are redundancy in a full set of atom positions. I discussed this issue in [Shirai18] (in Sec. V.C). This happens when there is energy degeneracy, namely, the same energy with different structures. We can save a tremendous number of state variables. However, in the present study, we are discussing which are state variables for solids. This investigation is particularly important, when recognizing that many people still believe that only T and V are independent state variables for solids too. Therefore, here I study the most general situation, in other words, the worst case. Degeneracy arises from symmetry, such as crystal symmetries, transposition symmetry, etc. Then, we can investigate how redundant degrees of freedom is removed. Please don't rush to investigate individual cases.

Q. 10 (Water case) *There are example cases that suggest reduced descriptions of glasses are indeed possible, i.e. where all $3N_a$ degrees of freedom*

are not required. See for example: N. Giovambattista, F. W. Starr, and P. H. Poole, *State variables for glasses: The case of amorphous ice*, *J. Chem. Phys.* **150**, 224502 (2019).

(A. 10) This point was already explained in question 9. Thank you for this interesting point. Yes, he is right. We do not need all atom positions. He suggests an interesting paper on water. In fact, I had read this paper, but I didn't cite this. The properties of water are very complicated, and hence many additional explanations about the background are needed when this topic is incorporated in this paper. In particular, when LDA and HDA of ice are discussed, people often argue the water issue in connection to the second critical point in the liquid state [Poole92, Poole97, Mishima98, Wilding06, Gallo16], which has not been verified experimentally. Presently, it is better not discussing this topics, because including this topics merely results in bringing confusion to the main logics of this study rather than helping to understand.

Q. 11 (Extensivity) *A state variable must be either extensive or intensive variable. But atom positions do not meet either additivity nor constancy by adding two subsystems.*

(A. 11) He posed a conceptual difficulty in the notions of extensive and intensive variables. Yes, there is difficulty. When macroscopic systems are treated, our judgment on whether extensive or intensive is based on the additivity of quantity: if the system is divided by half, the extensive variable of the original system is equal to the sum of those of the two parts. However, more careful consideration casts doubt to this simple judgement. Pressure is usually regarded as an intensive variable. However, for a mixed gases, the total pressure is equal to the sum of partial pressures of the components. In this regard, pressure has additivity. On the other hand, each of the component gases shares the same volume. The volume looks something intensive variable. Entropy is usually considered as an extensive variable. However, mixing entropy destroys the additive property. More examples are given in [Grandy08] (see ch. 5). Grandy described that the distinction is anthropomorphic: it depends on the particular kind of subdivision we choose to envision. After all, we see that the idea of extensivity is only approximation and is not a fundamental notion.

One gram of iron can be divided by half. The sum of the energies of the divided parts, U_1 and U_2 , gives exactly the energy of the original piece, U_0

$$U_0 = U_1 + U_2. \quad (6)$$

An interesting question is to what extent finely we can divide the system. For gas systems, the additive property holds up to the atomic level. The total energy of an ideal gas system is given by summing up the kinetic energy of all the gas atoms. For solids, the additivity may hold at the scale of micron meters or similar scales. However, at the atomic-size scale, it is not. We know that the total energy is not the sum of the energy of individual energy. For solids, even the idea of the energy of individual atom is not well defined. An extreme case is the entropy of black hole. The entropy of a black hole, S_{bh} is proportional to its surface area A but not to the volume, $S_{\text{bh}} \propto A$. The interaction inside the black hole is so strong that the additive property does not hold even at the macroscopic scale.

The notions of extensivity and additivity are actively debated in the front of research. For interacting-particles system, the extensivity and additivity do not hold. The fundamental question is how to determine the distribution function for particles [Press13, Press13a, Saadatmand20, Tsallis11, Tsallis15, Tsallis23].

In summary, I like to say that, for interacting systems, the total quantities are the most important. The total energy and total entropy are the most significant quantities. Sub-dividability holds only approximately, depending on the scale and the range of interactions.

Q. 12 (Uniqueness of the time average) *Definition 3 states that, if a dynamical variable has a definite time average, it is a state variable. However, for a gas in a box, the time average of a gas particle has a definite value of the center of mass. But, the center of mass is not a state variable. Therefore, Definition 3 is incorrect.*

(A. 12) For gas systems in a box, the position, $x(t)$, of a gas molecule is constrained within the wall. In equilibrium, the molecule visits everywhere in the box with equal probability. The time average of the molecule's position, $\overline{x(t)}$, has a definite value, namely, the center of mass. This result is trivial. All the molecules in the box have the same time average, and this time average has no relevance to the internal energy U . Thus, usually $\bar{x}$ is not a state variable. However, there is a situation that it comes to play in

thermodynamics. The thermodynamic properties of water do not depend on the elevation h at which we measure. The specific heat of water does not depend on h . However, in a hydroelectric power plant, the elevation of water is the most important variable to determine the power efficiency. It determines the potential energy of water as Mgh . As indicated in this example, the issue is the relevance to the current scope of problem. If the variable is not in the current scope, it is called *frozen coordinate*: it does not change within the scope in question. This issue is studied in [Shirai18]. This notion of frozen coordinate has a far-reaching consequence on the third law. The subject is studied in [Shirai22-res].

References

- [Bridgman50] P. W. Bridgman, Rev. Mod. Phys. **22**, 56 (1950).
- [Bridgman61] P. W. Bridgman, *The Nature of Thermodynamics* (Harper & Brothers, New York, 1961).
- [Callen85] H. Callen, Thermodynamics and an Introduction to Thermostatistics, 2nd Edition, Wiley, New York, 1985.
- [Davies53] R. O. Davies and G. O. Jones, Proc. Roy. Soc. A **217** 26 (1953).
- [DiMarzio76] E. A. DiMarzio, Annals New York Acad. Sci., **279**, 86, (1976)
- [DiMarzio76a] E. A. DiMarzio, J. H. Gibbs, P. D. Fleming-III, and I. C. Sanchez, Macromolecules, **9**, 763 (1976).
- [Gallo16] P. Gallo *et al.*, Chem. Rev., **116**, 7463 (2016)
- [Grandy08] W. T. Grandy Jr., *Entropy and the Time Evolution of Macroscopic Systems* (Oxford, Oxford, 2008).
- [Gyftopoulos05] E. P. Gyftopoulos and G. P. Beretta, *Thermodynamics - Foundations and Applications* (Dover Pub., New York, 2005).
- [Jaynes65] E. T. Jaynes, Am. J. Phys. **33**, 391 (1965).
- [Khinckin98] A. Y. Khinckin, *Mathematical Foundations of Quantum Statistics*, (Dover Pub., 1998)

- [Lebowitz83] J. L. Lebowitz, Phys. Today **46**, (9) 32 (1993).
- [Mandelbrot62] B. Mandelbrot, Ann. Math. Stat. **33**, 1021 (1962).
- [Mandelbrot64] B. Mandelbrot, J. Math. Phys. **5**, 164 (1964).
- [Mishima98] O. Mishima and H. E. Stanley, Nature **396**, 329 (1998).
- [Poole92] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature **275**, 322 (1992).
- [Poole97] P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, Science, **275**, 322 (1997).
- [Press13] S. Pressé, K. Ghosh, J. Lee, and K. A. Dill, Rev. Mod. Phys. 85, **1115** (2013).
- [Press13a] S. Pressé, K. Ghosh, J. Lee, and K. A. Dill, Phys. Rev. Lett. **111**, 180604 (2013).
- [Saadatmand20] S. N. Saadatmand, T. Gould, E. G. Cavalcanti, and J. A. Caccaro, Phys. Rev. E **101**, 060101(R) (2020).
- [Shirai18] K. Shirai, *State Variables and Constraints in Thermodynamics of Solids and Their Implications*, arXiv:1812.08977.
- [Shirai20] K. Shirai, J. Phys. Commun. **4**, 085015 (2020).
- [Shirai21] K. Shirai, J. Phys. Commun. **5**, 015004 (2021).
- [Shirai21a] K. Shirai, J. Phys. Commun. **5**, 095013 (2021).
- [Shirai22] K. Shirai, K. Watanabe, and H. Momida: J. Phys.: Condens. Matter **34**, 375902 (2022)
- [Shirai22-res] K. Shirai, *Residual Entropy of Glasses and the Third Law Expression*, arXiv: 2207.11421
- [Shirai23] K. Shirai, K. Watanabe, H. Momida, and S. Hyun, J. Phys.: Condens. Matter **35**, 505401 (2023).
- [Shirai24] K. Shirai, *Revisiting nonequilibrium characterization of glass: history dependence in solids*, arXiv:2406.15726.

- [Tisza63] L. Tisza, P. M. Quay, *Ann. Phys.* **25**, 48 (1963).
- [Tsallis11] C. Tsallis, *Entropy* **13**, 1765 (2011).
- [Tsallis15] C. Tsallis, *Entropy* **17**, 2853 (2015).
- [Tsallis23] C. Tsallis, *Entropy* **25**, 743 (2023).
- [Wark99] J. K. Wark and D. E. Richards, *Thermodynamics* 6th. ed (McGraw-Hill, Boston, 1999) p. 294.
- [Wilding06] M. C. Wilding, M. Wilson, and P. F. McMillan, *Chem. Soc. Rev.*, **35**, 964 (2006).