The inquiry of liquids and glass transition by heat capacity

Hai Bo Ke, Ping Wen, and Wei Hua Wang

Related Articles

Additional information on AIP Advances

The inquiry of liquids and glass transition by heat capacity

Hai Bo Ke, Ping Wen,[a] and Wei Hua Wang
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

Reconsidering the intrinsic connection between simple liquids and the glass transition, we attempt to understand them with an explicit liquid model. Liquids are defined to the mixture composed of tiny particles restricted in non-identical potential energy wells, where translational motions of tiny particles in statistical equilibrium, as well as vibrations and rotations, are distinguished. The liquid model offers an opportunity to build up a quantitative correlation between heat capacity and the basic motions appearing in liquids. Agreements between theoretical prediction and experimental data on heat capacities of typical simple liquids are reached. A serial of experimental data confirm that the glass transition originates from the falling out-of-equilibrium of the translational motions in liquids. The work might provide a novel and intuitive way to uncover a shady corner of the mysterious liquids and the glass transition. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4773224]

I. INTRODUCTION

Liquids are not only of vital importance for physics and chemistry, technology, but also for life. As yet, the understanding of liquid state is still a challenge on the view of the theoretical point.[1–3] In physics, the understanding of liquids involves the descriptions of structure, dynamical, and thermodynamic properties with the clarification of the size and shape of molecules, atoms, and the nature of the forces between them.[2] Idealized model for liquids is of importance to understand the real liquids since the model can establish a base or hypothetical substance to treat real properties of liquids mathematically and clearly.[1] Such idealized models for the solids and gases have been already built up.[4] For an ideal solid or a perfect crystal, idealized model offers that tiny particles (e.g., atoms or molecules) composing the matters execute only small vibrations around certain equilibrium position, *e.g*., the crystal lattice sites. For the ideal gas, idealized model tells us that each tiny particle without any interactions moves translationally throughout the volume in which it is contained. Extensions and corrections to these idealized models for describing real substances provide close agreement with experimental data. However, up to now, no idealized liquid model has been accepted since considerable difficulties may be fronted to describe the motions of the tiny particles in liquid. Liquids' inability to support any shearing[1] indicates that tiny particles or their clusters/groups in liquids can migrate through some fluctuations. This makes it inadmissible to treat liquids with the model of solids, even though liquids and solids (the so-called condensed matters) resemble each other in their strong interactions and high densities. On the other hand, the current gas model can not be applied to liquids, whatever a liquid may be considered as a dense gas, and both liquids and gases are often referred to as 'fluids'. Importantly, it is unacceptable to consider that a liquid exhibits intermediate properties between those of a solid and a gas. The difficulty to understand the liquids has been revealed by the fact that the heat capacity of liquid is not, or is barely, mentioned in physics textbooks as well as books related to liquids.[1–7] This thermodynamic property, the heat capacity, has been already known as the simplest and the most direct test of any theory since in statistical physics its calculation requires the fewest assumptions.

---

[a]Contact author, email: pwen@aphy.iphy.ac.cn

2, 041404-1

At constant pressure, a liquid covers not only the normal liquid range from its freezing point T_m to its boiling temperature, but also the undercooled range from T_m to the glass transition temperature T_g.[1,8–10] Like normal liquids, the undercooled liquids are also popular. Without the interference of the crystallization, almost all of liquids can exist until temperature is approaching to T_g. Upon cooling, across a narrow transformation range, liquids become rigid solids, glasses without any observable structural change. This phenomenon, termed as the glass transition, is one of the deepest theoretical problems in current condensed matter physics.[11] A puzzling basic dynamic feature related to the glass transition is that for most liquids only with few exceptions the temperature dependence of the structural relaxation time τ is non-Arrhenius as temperature decreases approaching to T_g.[8,12] Arrhenius fitting of τ requires that activation energy increases with decreasing temperature and appears to become infinite at a nonzero temperature T_0. It can not be explained by the normal rate theory with a constant energy barrier for any tiny particle to be overcome in the structural rearrangement. Influenced deeply by the critical phenomenon, most current models to the glass transition[9,10] predict that the slowing down is a consequence of an underlying or narrowly phase transition. Starting with realistic model of liquids, where the motions of tiny particles are related to a cage that is composed of the tiny particle and its neighbors, the idealized model-coupling theories[13,14] predicts that the undercooled liquids close to T_g is already out-of equilibrium since a dynamic phase transition occurs at around $1.2T_g$. In fact, the undercooled liquids are still in statistical equilibrium at least within the normal experimental time scales. Up to now, no any convincing evidences exhibit that there is a difference between normal liquids and undercooled liquids. Instead of querying the model, the undercooled liquids have been considered as special liquids since the cage model for normal liquids is useless any more.[8] Consistent with free volume theories,[15] the entropy model[16] assumes that cooperatively rearranging regions (CRR) are the basic units representing structural rearrangement in undercooled liquids. Upon cooling the increasing average size of CRRs, consistent with the decreasing free volume, gives a qualitative description to the feature of structural relaxation in viscous liquids. Currently, the idea of cooperatively rearranging region has a far-reaching impact on the understanding of the undercooled liquids. But CRRs in undercooled liquids, as well as the free volume, can not be confirmed by the experiments yet.[8,17] The undercooled liquids and the glass transition are so mysterious and attractive that lots of theoretical and experimental efforts have done.[9–11,18–20] However, the glass transition as well as the undercooled liquids is still beyond our understanding.

According to the basic principles in statistical physics, the heat capacity of a matter with an equilibrium state mirrors the possible motions of the tiny particles in the system.[4] That is, liquid heat capacity can reveal directly what kinds of motions of tiny particles in liquid are involved. The description of the heat capacity does not require the considerations of the actual dynamical processes related to the motions of the tiny particles. Therefore, the heat capacity of liquid, compared to complex liquid dynamical behaviors, can provide more important and impacting clue to understand the normal liquids, the undercooled liquids and the glass transition. However, there are few efforts to take into accounts the connection between the motions in liquids and heat capacity of liquids. Usually and always, liquid heat capacity has been explained with the complex inter-atomic or inter-molecular interactions. It has been argued pessimistically that no general expressions for liquid dynamics can be obtained since the interactions determining directly structural rearrangements in liquids are system-specific. Then, the current consideration of liquid heat capacity makes it sure that no general expressions exist for liquid heat capacity. Alike situation exists in the field of the glass transition. The excess heat capacity ΔC_P of undercooled liquids relative to their glass state has been described with the dynamics of viscous liquids.[16,20,21] So it is not strange to find that no consensus on the understanding of the ΔC_P even in qualitative level has been reached.[9,10,19,20]

There is a naïve question why heat capacity has a mathematical expression of a parameter characterizing the dynamic behavior of liquids. Clearly, thermodynamic properties and dynamic behaviors are two different aspects of the motions in a matter.[4] So different from conventional way, in this article, based on the previous works,[22–25] we manage to open the problem of the liquids and the glass transition with an explicit and simple liquid model. With the liquid model and the basic principles in statistical physics, the simple liquid heat capacity model is built up. The liquid and heat capacity models are found to apply well to some real simple liquids and a serial of glass forming

undercooled liquids. It is found that the natures of liquids and the undercooled liquids, as well as the glass transition, can be uncovered through the understanding of the translational motions in liquids. The result might offer a novel way to reveal a shady corner of the mysterious liquids and the glass transition.

II. MODEL OF SIMPLE LIQUIDS AND THEIR HEAT CAPACITIES

A. Model of simple liquids

A century of effort and advances in statistical mechanic (the fundamental formulations of Gibbs and Boltzmann, integral equations and perturbation theories) have led to a fairly basic understanding of the liquids. Liquids refer to a condensed matter made up of tiny particles that held together by chemical bonds. The positions of the tiny particles are random at any moment, and also varied with time. The chemical bond in liquids involves all types of bonds known, e.g., metallic, covalent, ionic and hydrogen bond. The interactions and local microstructures in knowledge of inter-particles force have made fairly precise predication of the solid-liquid-gas phase diagram,[2] even though the accurate calculation and prediction of properties of a real liquid over significant ranges remain unable.[26] The lack of idealized model is the key obstruction to describe and predict the properties of liquids.

The question now arises as to whether there is a universal description for all of types of liquids or not. The answer to this is positive. The first reason is that any tiny particles in liquids, the basic carriers of motions determining the intrinsic properties of liquids, can be simplified. It is known that atomic nuclei are much heavier than electrons. For atoms, it is useful to replace atomic motions by nuclear motions with bypassing the electronic problem completely. Electronic motions representing electronic transport properties are only taken care in some special liquids, and system-specific, and should be overlooked in the idealized liquid model. For molecules, the intermolecular interactions in liquids are often much weaker than intramolecular interactions between inner atoms inside molecules, meaning that any coupling between intramolecular motions and intermolecular motions does not exist. It is reasonable to replace complex molecular motions by the motions of molecule as a whole with bypassing the problem of intramolecular motions completely. The second reason is that the different bonds in liquids with wide spectra, belong to the Coulomb interactions, and are same in nature. Then the potential energy functions in liquids depend only on the positions of the tiny particles without considering the exact feature of the interactions. The third reason is that liquids with high density are in statistical equilibrium, indicating that any tiny particle is surrounded tightly by its neighbors at any moment, and the complicated interactions forced on any tiny particle can be replaced by a mean field. As a result, a general pattern for the situation of any particle in liquids can be reached. At any moment tiny particles in liquids is posited with a potential energy well. It is obvious that this pattern cannot be used for the tiny particles on the surfaces of liquids. Since the liquids considered here are bulk or macroscopic, the tiny particles on the surface relative to all of particles in the liquids are considerable few. It is reasonable to consider that the contributions of tiny particles on the surface to the properties characterizing bulk liquids are ignored.

With the existence of the potential energy well, the complicated motions of any atoms or molecules in liquids can be classified clearly into the well-known basic motions in physics. The first basic motions owning to the potential well are the vibrations of tiny particles in space. The feature of the vibrations in liquids is same as that in solids, where the tiny particles are also limited by a potential energy well. The existence of vibration of tiny particles in liquids is the intrinsic feature of liquids, which makes liquids distinct from gases. The rotations of tiny particles can also exist in liquids. But the rotation is only possible for the tiny particles that are far from spherical. Besides vibration and rotation, there is another important motion existing in liquids, which has been usually neglected purposely. The motion is the jumping of tiny particles away from its position in potential energy well. The jumping is characterized by a short free path that is around the distance between two possible neighboring particles in liquids. Different from vibration, the jumping contains only the energy level of kinetic energy. In theory, there is no intrinsic difference between the jumping in liquids and the translational motion in gases if the length of their free paths is not considered. Therefore, in order to avoid concept confusion, the jumping motion with a potential energy well in

liquids is also termed as translational motion. The translational motion must not be confounded with the vibration. Vibration in liquids takes only place in a potential energy well. In classical physics, the vibrational energy level contains the combination of kinetic energy and potential energy. One must realize that it is insufficient to describe the energy level of vibration with kinetic energy. This is the intrinsic difference between translational motion and vibration in liquid.

Compared with idealized solids, ideal liquids are characterized by the translational motions. The translational motion in liquids is localized, and arisen from thermal activation. Without any external field (the gravitational field, compared with thermal energy at high temperature, is too weak to be considered), the residual translational motion time t at a given temperature T has the form $t(T, \Delta E) = \tau_0 \exp[\frac{\Delta E}{k_B T}]$, where k_B is Boltzmann constant and τ_0 is a typical microscopic time around 10^{-13}. Correspondingly, whether the translational motion can be observed actually or not depends not only on the thermal energy to overcome the energy barrier accompanied by the potential energy well, but also on the probing time. At normal condition, the probing time is in the orders of several seconds, and much longer than the residual times related to translational motion in normal liquids, where the thermal energy $k_B T$ (corresponding to the temperature in normal liquid region) relative to the barrier energy is high and the average residual translational motion time is much shorter than the usual probing time. Therefore, with the normal probing time the transitional motion in normal liquids is in statistical equilibrium, and the liquids can not bear any shear. On the other hand, when the probing time is much shorter than the residual translational motion time in liquids, the liquids is solid-like.[10] It is known that liquids have the instantaneous elastic modulus.[10] Therefore, distinguishing from rigid solids, liquids are defined here as the condensed matter with disordered microstructure, where the translational motions for all of tiny particles are in statistical equilibrium.

It is emphasized here that the intramolecular motions overlooked in the above liquid model are restricted to inner atoms insider molecules, but inner atomic groups inside molecules. The motions of inner atomic groups inside the molecule in liquids have effects on the motions of the molecule as a whole. One will find the effects of the motions of inner atomic groups inside the molecule in liquids can be remedied easily by the extension of the above liquid model.

B. Liquid heat capacity

The model of simple liquids offers an opportunity to describe quantitatively the heat capacity of simple real liquids. We make the first aim to the heat capacity of liquids containing only spherical particles. With the ignoring of the motions insider the particles in these liquids, there are only two types of basic motions: vibration and translational motion. Correspondingly, the energy of a given particle in the liquids is written in the form as $\varepsilon = \varepsilon_0 + \varepsilon_{vib} + \varepsilon_{trans}$, where ε_0 denotes the energy levels internal state of the atom and is independent of the vibration, translation and coordinates of the centre of mass of the atom. ε_{vib} and $\varepsilon_{\text{trans}}$ refers to the energy level of atomic vibration and translation, respectively.

The vibrations in the potential energy well are harmonic. Its energy levels ε_{vib} is given by the usual expression $\hbar\omega(n + \frac{1}{2})$, where $\hbar\omega$ is the vibrational quantum, and n is the vibrational quantum number. In statistical physics,[4,5] the calculation of vibrational contribution C_V^{vib} to heat capacity at constant volume is elementary. Vibrational partition function Z_{vib}, owing to the very rapid convergence of the series, is given as, $Z_{vib} = \sum_{n=0}^{\infty} e^{-3\hbar\omega(n+1/2)/k_B T} = 1/(1 - e^{-\hbar\omega/k_B T})^3$, where the number of 3 refers to three independent harmonic oscillators for the vibration of one particle in a potential energy well. Then the average energy related to the vibration is written as, $\bar{E} = -\frac{\partial \ln Z}{\partial (1/k_B T)} = 3\hbar\omega/(e^{\hbar\omega/k_B T} - 1)$, and the C_V^{vib} contributed from the vibration of one particle is $C_V^{vib} = \frac{\partial \bar{E}}{\partial T} = 3k_B(\frac{\hbar\omega}{k_B T})^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T}-1)^2}$. In liquid region, thermal energy $k_B T$, compared with $\hbar\omega$, is usually much higher. That is, the function, $\hbar\omega/k_B T \ll 1$, is tenable. Hence, in liquids C_V^{vib} is of temperature-independence, and close to $3k_B$ per one particle, and $3R$ (R is gas constant) per molar particles.

The energy level of translational motion is given by classical physics as follow, ε_{trans} $= c_x p_x^2 + c_y p_y^2 + c_z p_z^2$, where p represents momentum, x, y, and z denotes the coordinates, c refers a constant related to momentum. It is appropriate to assume that the values of p are discretely spaced, separated by small interval Δp that is much less than $k_B T$, since the energy barrier related to the translational motion in liquids has a wide and continuous distribution. The translational partition function Z_{trans} is written as, $Z_{trans} = \sum_{p_x, p_y, p_z=0}^{\infty} e^{-\frac{c_x p_x^2 + c_y p_y^2 + c_z p_z^2}{k_B T}}$. Based on the known mathematical treatment, the final forms for the Z_{trans} is, $Z_{trans} = C(k_B T)^{3/2}$, where C is an abbreviation for $\frac{\sqrt{\pi^3/c_x c_y c_z}}{\Delta p_x \Delta p_y \Delta p_z}$. Then the average energy related to the translational motion is $\bar{E} = -\frac{\partial \ln Z}{\partial (1/k_B T)} = \frac{3}{2} k_B T$, and the corresponding C_V^{trans} arisen from translational motions of one particle is $C_V^{trans} = \frac{\partial \bar{E}}{\partial T} = \frac{3}{2} k_B$, and is also independent of temperature. This is just the equipartition theorem.

As a result, according to our simple liquid model, the C_V of liquids containing only spherical particles is a sum of C_V^{vib} and C_V^{trans}:

$$C_V = C_V^{vib} + C_V^{trans}, \tag{1}$$

The C_V of liquids is independent of temperature and equal to $4.5R$ per molar particles. It is usual, in theoretical considerations, to ignore the difference between heat capacity C_P at a constant pressure and C_V for a condensed matter; this neglect involves only small errors, and can be remedied if the accuracy of the theory should warrant it.[27] Hence, the value of C_P in the simple liquids containing spherical particles is close to $4.5R$ per molar particles.

Next, we study the heat capacity for the liquids composed of non-spherical particles. In order to simplify the situation considered, we firstly take aim on liquids, where no complex inner segments, such as $-CH_2-$, $-CH-CH_3-$, and so on, exist inside the particles. This means that no consideration of the motions related to inner segments inside the particles is needed. According to the simple liquid model, the simple particle as a whole in liquids has three types of motions: vibration, rotation and translation. Correspondingly, heat capacity C_V is a sum of vibrational contribution C_V^{vib}, rotational contribution C_V^{rot}, and translational contribution C_V^{trans}:

$$C_V = C_V^{vib} + C_V^{rot} + C_V^{trans} \tag{2}$$

The calculation of is same as that in liquids containing spherical particles, and its value is independent of temperature and close to $3R$ per molar molecules. The rotational contribution C_V^{rot} to the heat capacity in a liquid can be derived by the method used in a gas.[4] In normal liquid region, C_V^{rot}, independent of temperature, is close to $iR/2$ per molar molecules. The value of i, the number of rotational degrees of freedom, depends on the fine structure of the molecule considered.

Different from the translational motions of spherical particles, the translational motions for non-spherical particles in liquids are a little complicated. The spherical particle only has one form to move translationally, but there are more than one possible form for non-spherical particle to move translationally in liquids. With the above liquid model, it is clear that vibration, rotation, and translational motion for the non-spherical particles in liquids must take place at a different time scale. Along the probing time, vibration takes place firstly and quickly. As the probing time prolongs, rotation happens. With further prolonging time, translational motion appears. Clearly, translational motion is accompanied by rotation, but vibration. After the translational motion is finished, that is, the particle jumps into another potential energy well, the above evolvements of the motion starts to repeat again. This evolvement of the motion in liquids can be confirmed by several experimental facts. It has been found that molecular rotation may persist in a crystal[28,29] and the relaxation time of molecular rotation is shorter than that of the translational motion in liquids.[30–33] Then the rotation in liquids, but the vibration, has an effect on the phase space of translational motion. In other words, without the consideration of inner motions insider particles, rotation affects the possible forms of particles to move translationally. Rotation in liquids can be treated by classical physics since temperature in liquid region relative to rotational quantum ($\frac{\hbar^2}{2k_B I}$, I is the moment of inertial of the molecule) is much higher. According to equipartition theorem,[4,34] it is appropriate to think that the number of the particle translational forms arising from its rotation is equivalent to the number

of rotational degrees of freedom. Correspondingly, the energy level of the molecular translational motion is given clearly as follow,

$$\varepsilon_{trans} = \sum_i \left(c_{xi} p_{xi}^2 + c_{yi} p_{yi}^2 + c_{zi} p_{zi}^2 \right), \tag{3}$$

where p represents momentum, x, y, and z denotes the coordinates, i is the number of translational forms. Obviously, the values of i are 2 for a diatomic molecule, and to 3 for a polyatomic molecule. With the known mathematical treatment, one can find that the translational contribution C_V^{tran} to the heat capacity in a liquid containing one mole particles is equal to $\frac{3}{2} i R$. Therefore, without the consideration of the contribution arisen from the internal state of the non-spherical particles, the liquid heat capacity C_V, as well as C_P, is the sum of C_V^{vib}, C_V^{rot}, and C_V^{tran}, and is equal to $3R + \frac{i}{2} R + \frac{3}{2} i R$ and invariable with temperature.

Without consideration of the contribution related to atomic vibrations inside the non-spherical particle is too simplified. In practice, for many simple molecules in liquids, the inner atomic vibration usually can not be ignored since temperature in liquid region relative to inner atomic interaction is usually considerably high. Assume the temperature in liquid region is not large enough to excite the very high vibrational level, the atomic vibration insider a molecule should be harmonic, and its energy levels can be given by the usual expression, $\hbar\omega(n + \frac{1}{2})$. The contribution of the vibrations of one atom in one dimension has the form as follow,

$$C_{V,a}^{Vib} = \left(\frac{\hbar\omega_a}{k_B T} \right)^2 \frac{e^{\hbar\omega_a/k_B T}}{(e^{\hbar\omega_a/k_B T} - 1)^2} = f(\hbar\omega_a/k_B T), \tag{4}$$

where $\hbar\omega_a$ is the vibrational quantum, and a denotes given atom in the molecule. It is clear that $C_{V,a}^{Vib}$ increases with increasing temperature, and approaches to k as temperature is higher than $\hbar\omega_a/\kappa$. The exact total values of $C_{V,a}^{Vib}$ for one the particle in liquid state requires the understanding of the fine structure of the molecule. Finally, the total heat capacity C_V or C_P of a simple liquid containing one mole molecule is given in the form:

$$C_{V,P} = 3R + \frac{i}{2} R + \frac{3}{2} i R + \sum_a N_A n_a f(\hbar\omega_a/kT), \tag{5}$$

where N_A is Avogadro's number (6.022×10^{23}) and n_a is the number of the bonds related to a atom. The third part in C_V is the integral of all of atomic contribution inside the particle. It should be emphasized that the value of i the above equation can be only applied for simple liquids composed of non-spherical particles.

For the liquids composed up of non-spherical particles with complex fine structure and molecular segments, certain extensions and modifications must be added with the possible motions arising from inner molecular segments. It is still possible to describe quantitatively the heat capacity of the liquids on the basis of the known molecular fine structure with the above method.

III. THE MODEL OF GLASS TRANSITION

All current models[9–11, 13–16, 18–20] related to the glass transition remain vague to a certain degree. It may be useful to reconsider the glass transition with the above liquid understanding. Firstly we notify that the above liquid model is still applied well for undercooled liquids. The fact is that microstructure of liquids in whole region involving normal and undercooled liquids varies little with temperature, and no intrinsic change in the microstructure can be found as a glass is formed upon cooling.[35] This indicates a possibility that the interactions and the carriers of the motions in liquids do not change in nature as temperature is decreasing from T_m to T_g. According to our liquid model, it is clear that the intrinsic difference between liquid and solid is whether the translational motion in statistical equilibrium is available or not within the probing time. Hence, it can be pointed out that the mysterious glass transition in nature is related directly to the temperature and time dependence of the translational motions in liquids.

In the time domain, the dynamics of liquids correlated to translational motions can be described qualitatively by model of traps.[36,37] Any transitional motion in liquid, as an independent thermal
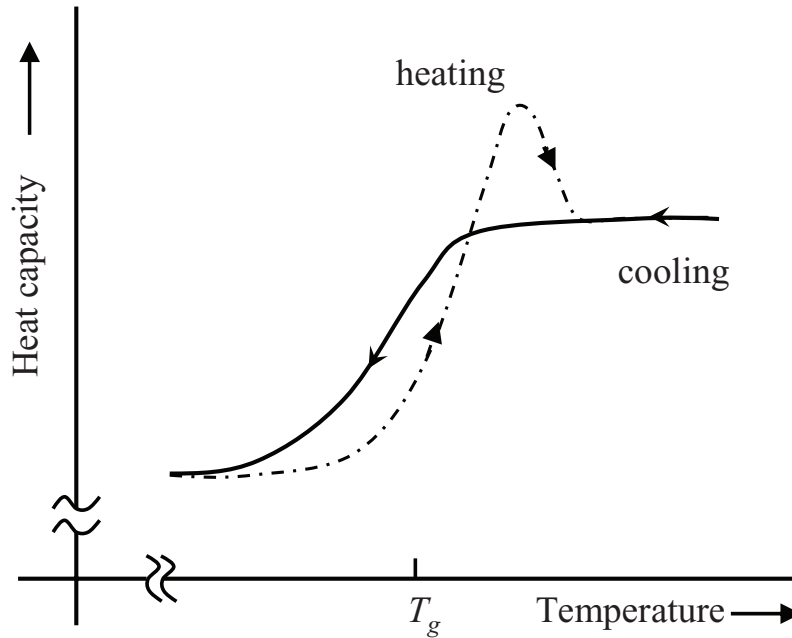
FIG. 1. Thermogram near the glass transition temperature T_g.

activation event, is characterized by its energy barrier ΔE. The probability distribution of ΔE is defined as $\rho(\Delta E)$. In this picture, the response function at a given temperature T can be viewed to be a good approximation as arising from a probability distribution $\rho(\Delta E)$, $\phi(t) = \frac{\sigma(t)-\sigma(\infty)}{\sigma(0)-\sigma(\infty)}$ $= \int e^{-t/\tau(\Delta E)}\rho(\Delta E)d\Delta E$, where $\tau(\Delta E)$ is the relaxation time ($\tau(\Delta E) = \tau_0 \exp[\frac{\Delta E}{k_B T}]$, τ_0 is a typical microscopic time around 10^{-13}) and σ is the measured quantity. This response function resembles KWW function[38] ($\phi(t) = \exp[-(\frac{t}{\tau})^\beta]$) with the β parameter, whose value is no more than one. The value of β is determined by the explicit form of $\rho(\Delta E)$. This non-exponential relaxation from solid to liquid behavior is a basic feature of viscose glass forming liquids.[11,39] The temperature dependence of the average translational relaxation time should depart from Arrhenius form. The average energy barrier ΔE of translational motions, corresponding to the potential energy wells in liquids, depends on temperature at constant pressure. This temperature dependence arises from the effect of anharmonic interactions in liquids (expansion with heating and contraction with cooling). For a certain approximation, the ΔE for the translational motions in liquids enlarges with decreasing temperature. This is another feature of viscose glass forming liquids.[11,12] The prolonging of the average translational relaxation time with decreasing temperature makes it inevitable that liquids without crystallization become finally rigid solids, owning to the falling out of statistical equilibrium of the translational motion as temperature is lower enough. This can be observed in temperature window upon cooling.

Consistent with above description, the origin of glass transition can be displayed well by the change of heat capacity in the time and temperature window. In the time window, when the probing time is larger enough than the average translational relaxation time, liquids as a whole is in statistical equilibrium, and the heat capacity contains the contributions from transitional motions. On the other hand, when the probing time is shorter enough than the average translational relaxation time, the contribution of translational motions is not observed. A heat capacity step of $\frac{3}{2}iR$ for simple molecular liquids, and $\frac{3}{2}R$ for atomic liquids in time or frequency window is displayed. In fact, this change of heat capacity in time window is not popular. On the other way, heat capacity step has been usually shown in temperature window (see Fig. 1). A continuous step in heat capacity appears across the glass transition. Clearly, the heat capacity step originates from the falling out-of-equilibrium of translational motion in liquids in temperature window. The value of the heat capacity step must be

TABLE I. Molar heat capacities at constant pressure, C_P, for liquid elements.[40]

Element	C_P (JK^{-1}mol^{-1})	Temperature range (K)
Be	29.46	1560–2800
Mg	32.64	922–1150
Al	31.8	933–2400
Ca	29.29	1112–1757
V	47.49	2175–2600
Cr	39.33	2130–
Mn	46.0	1517–2333
Fe	41.8	1809–1873
Co	40.38	1768–1900
Ni	38.49	1726–2000
Cu	31.38	1356–1600
Zn	31.38	693–1200
Se	35.1	493–800
Y	39.79	1799–2360
Ag	30.54	1234–1600
Te	37.7	723–873
Ce	37.7	1071–1500
Pr	42.97	1204–1500
Nd	48.79	1289–1400
Ta	41.8	3250–4000
Au	29.29	1336–1600
Tl	30.1	577–1760

same as that observed in time or frequency window. The accumulated experimental data on the heat capacity step at T_g will offer a good test for the understanding of the glass transition.

IV. EXPERIMENTAL EVIDENCES

A. Heat capacity of simple liquids

1. Liquid metals

In theory, liquid metals have been considered as ones of the simplest liquids. Atoms in liquid metals can be treated as hard, inert spheres, which offer a relatively clear picture to understand their properties. It has been found empirically that the influence of temperature on liquid metal C_P tends to be small for most liquid metals. In general, the values of C_P are considered as a constant over relatively wide ranges of temperature. Heat capacities at constant pressure for several liquid metal elements have been summed by Kubaschewski and Alcock.[40] In Table I, most liquid metals have C_P values ranging from 30 to 40 Jmol^{-1}K^{-1} (3.6 $\sim$ 4.8R). The average C_P for these liquid elements is close to 4.5R. According to our liquid model, atomic vibrational contribution C_V^{vib} in liquids is close to 3R per mole atoms, and independent of temperature. No atomic rotational effect on thermodynamic properties needs to be considered. Any atom in metallic liquids only has one form to move translationally. Then the translational contribution C_V^{tran} is $\frac{3}{2}R$ per molar atoms, which is also independent of temperature. So the C_P of liquid metallic elements contains two parts: atomic vibrational contribution C_V^{vib} and atomic translational contribution C_V^{tran}. The sum of these two parts is 4.5R, which is independent of temperature. The constant atomic C_V^{vib} in liquid region is reasonable. According to the theoretical works of Einstein and Debye,[41,42] the vibrational contribution C_V^{vib} for atoms limited with a potential energy well must be close to 3R per mole atoms, and not influenced any more by the high temperature when temperature or thermal energy relative to the interaction is high. Therefore, even though accurate data for the heat capacities of liquids metals are not abundant and there is insufficient experimental data available to allow the temperature dependence of C_P to be
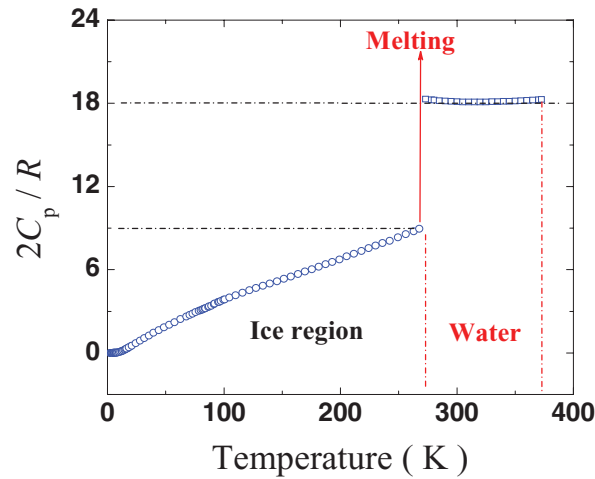
FIG. 2. The temperature dependence of the reduced heat capacity $2\Delta C_P/R$ (R, gas constant) for normal ice and water at ambient pressure.

determined, the empirical experimental data for liquid metal elements have already offered a good test for our proposed liquid model.

2. Water

As one of the most important condensed matters in our planet, water is composed up of the well-known compositional unit, H_2O molecule. The molecule has been considered as a rigid bent because the thermal energy can not activate the atomic motions inside the molecule in its normal liquid temperature region from 273 to 373 K at ambient pressure. Water, a pretty simple condensed matter molecular system, provides a good model system to test our liquid model and understand the real molecular liquids.

Heat capacity C_P of water at ambient pressure has been measured accurately. Usually, in the temperature region from 273 to 373 K the temperature dependence of the C_P (JK^{-1} mol^{-1}) is described by a Shomate equation, $C_P = -203.606 + 1.523 \cdot T - 3.196 \times 10^{-3} \cdot T^2 + 2.474 \times 10^{-6} \cdot T^3 + 3.855 \times 10^6 \cdot T^{-2}$.[43] In fact, as Fig. 2 displays, the heat capacity C_P at ambient pressure for one molar of H_2O molecules in its normal liquid temperature region is independent of temperature within the experimental error, and close to $\frac{18}{2}R$. The accurate description to the temperature-independence of C_P for water remains unable, even though it has been recognized since the discovery of the hydrogen bond that the properties of water own their existence to hydrogen bonds between water molecules. According to our liquid and heat capacity model, the origin of the C_P of water is apparent. Due to the existence of hydrogen bonds, any water molecule, except the molecules on the surface that are considerable few relative to those in the bulk, must be surrounded by its neighbor water molecules. This situation makes it sure that any water molecules posit in a potential energy wall at any given moment. So any water molecule in liquid can vibrate, rotate and move translationally. The C_P of water represents these different types of molecular motion. It is clear that the C_V^{vib}, the C_V^{rot}, and the translational contribution C_V^{tran} are $3R$, $1.5R$, and $4.5R$, respectively since the number of rotational degrees of freedom for H_2O molecule is 3. The sum of these contributions to C_P is $9R$, which is exact equal to the experimental data.

The temperature-independence of the C_V^{vib} and C_V^{rot} in water can be understood in details by the clarification of ice C_P. Any H_2O molecule in ice, as well as that in liquid, is also restricted by a potential energy well. There are some exact differences of the exact potential energy wells for H_2O molecule in between ice and water. But the difference can not change the possibility of the molecular motions fixed by the energy well. According to the understanding of the possible molecular motions in ice, ice C_P can be described well. With the previous experimental data,[44–46] ice C_P in Fig. 2 is found to increase gradually from 0 to $\frac{9}{2}R$ as temperature increases from 2 up to T_m of 273 K.
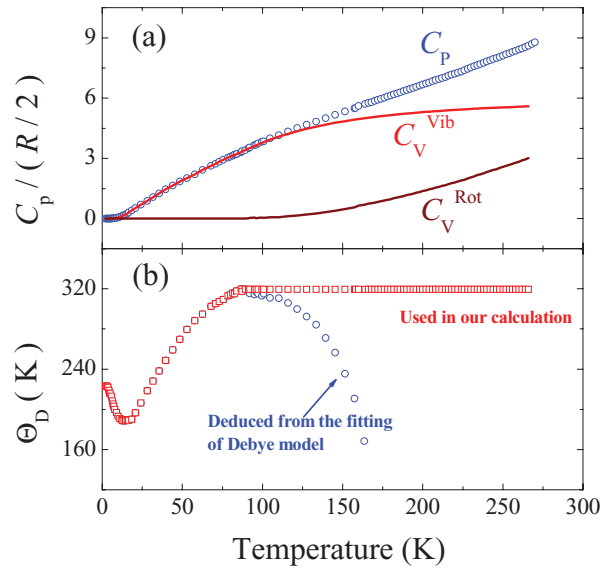
FIG. 3. (a) The separation of the C_P of ice into two parts: the C_V^{Vib} arisen from H_2O molecular vibration and C_V^{Rot} related to H_2O molecular rotation. The C_V^{Vib} is calculated by Debye model with the Debye temperature Θ_D marked with red color in Fig. 2(b); the black line is the C_V^{Rot} derived by the form, $C_P - C_V^{Vib}$. (b) The temperature dependence of the Θ_D in ice.

Apparently, the ice with N H_2O molecules contains $3N$ molecular oscillators. According to the empirical method,[47] the C_P^{vib} is given by the Debye form $C_V^{Vib} = 9Nk_B(\frac{T}{\Theta_D(T)})^3 \int_0^{\Theta_D(T)/T} \frac{x^4 e^x}{(e^x-1)^2}dx$ with the temperature-dependence of Debye temperature $\Theta_D(T)$. The values of the Θ_D determined by the best fitting are plotted in Fig. 3(b). Θ_D decreases firstly to a minimum at around 13 K, and then increases to a maximum at about 86 K as temperature increases from 2 K. When temperature is higher than 200 K, Debye model can not describe the experimental data any more. This means it is insufficient to think ice C_P composes only C_P^{vib}. In order to deduce the other possible contribution to ice C_P, we suggest that the Θ_D varying with temperature below 87 K is the intrinsic feature of the molecular vibrations. These vibrations related to the complicated molecular interactions cannot be fitted to the idealized solid model, Debye's solid model. The departing from a single value for Θ_D in low temperature region is normal for crystals.[47,48] Above 87 K the Θ_D is set to a single value as the maximum (319.3 K). This is consistent with the finding that the thermal motion of oxygen atoms in ice can be described by a single Debye characteristic temperature in the range from 183 to 273 K.[49] Even though the value of 319 K for Θ_D is a little higher since the melting point of the normal ice at ambient pressure is only 273 K, it is still reasonable. The reason is that the melting point and Θ_D are determined by the different interactions in ice. T_m of ice represents the interaction related to the tetrahedral molecule-clusters that have been considered as the basic structure of normal ice.[50] However, the Θ_D with high value corresponds to the stronger interactions accompanied by the local structure of "plane"-hexagonal H_2O molecule-array in ice. The interactions in the array are much stronger than those in the tetrahedral cluster. The local H_2O molecule-array has been found in water at high temperature region, while the tetrahedral cluster disappears as soon as the appearance of water.[51] Then the temperature dependence of C_V^{vib} [see Fig. 3(b)] can be calculated by above empirical Debye function, and the corresponding remaining heat capacity (C_P-C_V^{vib}) in ice is deduced [see Fig. 3(a)]. The remaining heat capacity increases monotonously from 0 to $\frac{3}{2}R$ as temperature increases from 90 to 273 K, and represents the evolvement of H_2O molecular rotations in ice.

The gradual increasing of the remaining heat capacity uncovers a secret in the ice. It is known that the vibrational contribution C_V^{rot} for one molar free H_2O molecules is $\frac{3}{2}R$ when temperature is higher than $\frac{\hbar^2}{2k_B I}$ ($\hbar$ is reduced Plank constant, I is the moment of inertia of H_2O molecule) since its rotation has three degrees of freedom in space.[4] The value of I for H_2O molecule is higher than
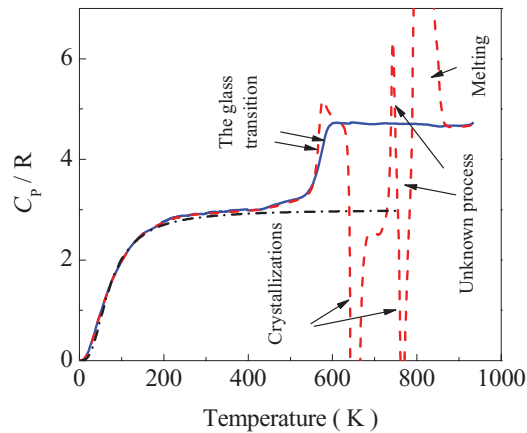
FIG. 4. The heat capacity C_P of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass former. The dash line is the C_P of the glassy sample measured during a heating; the solid line is measured during the cooling of 20 K/min from 950 K, the short dash line is the C_V calculated by Debye model with Debye temperature of 295 K.

1.0×10^{-47} kg·m^2.[52] Thus, the C_V^{rot} in theory is $\frac{3}{2}R$ only when temperature is higher than 40 K. In fact, H_2O molecules in ice are not free, but restricted by four nearest H_2O molecules with hydrogen-bond. In ice, there is an energy barrier for any molecular rotation. Correspondingly, the temperature (the thermal energy) needed to activate H_2O molecule rotator must be higher than 40 K. This is why the remaining heat capacity in Fig. 3 departs only from 0 at temperature around 90 K. It is reasonable to conclude that one rotator will contribute $\frac{3}{2}k_B$ to heat capacity as soon as the restriction of the rotator is overcome by thermal energy. So the increase in the remaining heat capacity in ice reveals that the number of H_2O molecules to rotate freely in ice increases continuously with increasing temperature. As temperature is approaching to 273 K, all of molecules are activated to rotate freely, and the rotational contribution is $3R/2$.

As a result, the quantitative description of the C_P of water and ice offers another test to the liquid and its heat capacity models, and provides a clear picture to the evolvement of the motions for H_2O molecules in the corresponding condensed matter. Within a potential energy well, H_2O molecular vibration activated by thermal energy takes place firstly. With increasing temperature or thermal energy, H_2O molecular rotations appear gradually. Only when temperature is up to a certain temperature that is determined by the intrinsic interactions in the system, all of the molecular rotators can be available. As temperature increases into liquid region, H_2O molecular translational motions in statistical equilibrium are observed. The translational motion is accompanied by the rotation. In normal water region, the constant C_P representing all of H_2O molecular motions in statistical equilibrium contain three temperature-independent parts: C_V^{vib} ($3R$), C_V^{rot} ($1.5R$) and C_V^{tran} ($4.5R$).

3. Undercooled liquid metal

As well as liquid metal elements and water, undercooled liquid metals are the important simple systems to understand what liquids are. Until recent, with the appearance of bulk metallic glass former undercooled liquid metals are available popularly. Bulk metallic glasses[53] are much more stable up to temperatures well above T_g, and allow accurate measurement of the properties above T_g without intervening crystallization.[54–57] Even that, only the special bulk metallic glass-forming alloy, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, can make it possible to measure the heat capacity of liquid metal in whole undercooled liquid region.[58]

Figure 4 shows the specific heat (C_P) of the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass former in the temperature region covering the solid, undercooled liquid and normal liquid region. During the cooling, no crystallization is found. On the other hand, several complicated crystallizations are observed in the heating curves. This unsymmetrical phenomenon of the crystallization in liquid metals has been explained by the separation between nucleation and growth processes in the temperature region.[59] Compared that measured during heating, the C_P of the metallic liquid measured during cooling is

more reliable. It is found that during the cooling the C_P is almost independent of temperature in the whole liquid region. The value of the C_P is around 4.7R. This finding is a little surprising. According to the conventional idea of the glass transition, the undercooled liquid, especial its supercooled liquid at temperature close to T_g, must be different from its normal liquid. But this observation is consistent with our understanding of liquids and the corresponding heat capacity. Without the consideration of electronic motions, it is sufficient to connect heat capacity of the liquid metal with atomic vibrations and atomic translational motions. In an equilibrium state, the contribution C_V^{vib} of atomic vibrations is 3R per mole atoms, and the C_V^{trans} arisen from atomic translational motion is 3R/2 per mole atoms. Their sum (4.5R), independent of temperature, is close to the experimental result on a certain degree, meaning that our models can be applied well for metal liquids in a wide liquid region.

The constant atomic vibrational contribution C_V^{vib} in the liquid metal can be confirmed by the T-dependence of C_P of the metallic glass. Fig. 4 shows the C_P of the metallic glass existing at temperature below T_g (550 K). Without the consideration of thermal effect of free electron, we can fit the C_P with Debye formula with a single Debye temperature Θ_D on a certain degree. The best fitting with the Θ_D of 290 K in Fig. 4 describes well with the experimental data in the temperature region below 430 K. This indicates that it is sufficient to consider only the atomic vibrations in the rigid solids, the glass and corresponding crystals. There is a departure of the fitting when temperature is higher than 430 K. The departing arises possibly from the existence of a few atomic translational motions in the glass at the higher temperature. In the metallic glass, it has been found that there is an obvious structural mechanical relaxation existing in the temperature region close to T_g.[19] Clearly this relaxation represents the atomic translational motions since translation motion is the only mechanism to the relaxation in metallic glasses. However, the departure in Fig. 4 is a little. So the consideration that atomic vibration is dominative motion in the metallic glass is still reasonable. Since the value of Θ_D (around 290 K) is much less T_g (550 K), it is appropriate to think that atomic vibrations are already in statistical equilibrium as temperature is approaching to T_g. Correspondingly, atomic vibrations in the metallic liquids have been already in equilibrium, and contribute 3R to the C_P.

Figure 4 also exhibits important clue to the origin of the glass transition in the metallic glass former. In the cooling curve the C_P observed decrease gradually across the glass transition. The step in the C_P is around 1.5R. This value is connected well with the falling out-of-equilibrium for all of atomic transitional motions in liquids. This finding supports our understanding of the glass transition. This understanding needs more evidences from different supercooled liquid metals to support.

B. Heat capacity related to the glass transition

1. Heat capacity step at T_g for metallic glass formers

It is difficult to measure the heat capacity step in time window for metallic undercooled liquids, even though the current metallic glass formers have a considerably stable undercooled liquid region. Usually it is much popular to determine heat capacity step across the glass transition upon heating in temperature domain. Figure 5 plots the heat capacity step ΔC_p across the glass transition and T_g for 45 kinds of metallic GFLs. The ΔC_P is determined by the heat capacity difference between the supercooled liquid and glass at T_g.[60] The compositions of the metallic glass formers are listed in Table II. It is found that the value of $\frac{2\Delta C_P}{R}$ is distributed around 3 with a narrow error of 10%, while the corresponding T_g is dispersed widely from 300 to 700 K. This finding in the metallic glass formers means that the ΔC_P of metallic GFLs is independent of the composition and equal to a constant, $\frac{3}{2}R$. The constant ΔC_P in metallic glass formers is contrary to the empirical pattern for the ΔC_P in glass formers,[21,61] in which the ΔC_P at T_g depends on the dynamics of the glass forming liquids. The larger the ΔC_P is, the more fragile the liquid is. We have found that the fragility values of these metallic glass-forming liquids depend on the composition of the system, and vary in a narrow region from 30 to 60.[55] However, the ΔC_p in the metallic glass formers can be described quantitatively by our models of liquids and the glass transition. The origin of the glass transition in these metallic glass formers is the falling out-of-equilibrium of all of transitional motions in liquid metals. This falling is accompanied by a heat capacity step, whose value of the step is equal to C_V^{trans}
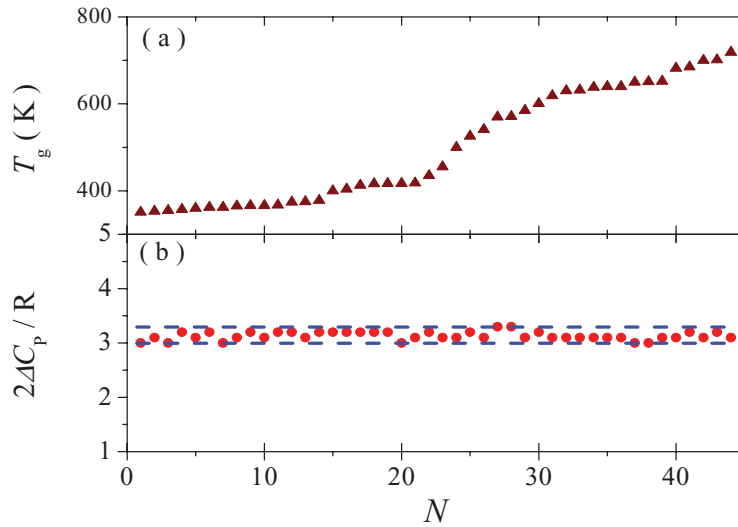
FIG. 5. (a) Plots of the glass transition temperature T_g *versus N* (the number of the metallic GFLs in Table I), (b) The reduced excess heat capacity $2\Delta C_P/R$ (*R*, gas constant) *versus N*.

TABLE II. The molar excess specific heat, ΔC_P, at T_g for 45 kinds of metallic glass formers. T_g is the onset glass transition temperature measured during the heating at 20 K/min. *R* is gas constant.

N	Name	T_g (K)	ΔC_P (JK^{-1}mol^{-1})	$2\Delta C_P/$ R	N	Name	T_g (K)	ΔC_P (JK^{-1}mol^{-1})	$2\Delta C_P/$ R
1	$Ce_{68}Al_{10}Cu_{20}Co_2$	351	12.6	3.0	24	$Pr_{55}Al_{25}Co_{20}$	500	12.7	3.1
2	$(La_{0.1}Ce_{0.9})_{68}Al_{10}Cu_{20}Co_2$	353	12.7	3.1	25	$La_{55}Al_{25}Co_{20}$	526	13.4	3.2
3	$(La_{0.2}Ce_{0.8})_{68}Al_{10}Cu_{20}Co_2$	355	12.6	3.0	26	$Nd_{55}Al_{25}Co_{20}$	541	12.8	3.1
4	$(La_{0.3}Ce_{0.7})_{68}Al_{10}Cu_{20}Co_2$	357	13.5	3.2	27	$Pd_{40}Ni_{40}P_{20}$	570	13.7	3.3
5	$(La_{0.4}Ce_{0.6})_{68}Al_{10}Cu_{20}Co_2$	360	12.9	3.1	28	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	571	13.7	3.3
6	$(La_{0.5}Ce_{0.5})_{68}Al_{10}Cu_{20}Co_2$	362	13.4	3.2	29	$Sm_{40}Y_{15}Al_{25}Co_{20}$	585	12.7	3.1
7	$(La_{0.6}Ce_{0.4})_{68}Al_{10}Cu_{20}Co_2$	362	12.5	3.0	30	$Gd_{55}Al_{25}Co_{20}$	601	13.4	3.2
8	$Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$	365	12.9	3.1	31	$Tb_{55}Al_{25}Co_{20}$	619	12.9	3.1
9	$(La_{0.8}Ce_{0.2})_{68}Al_{10}Cu_{20}Co_2$	366	13.1	3.2	32	$Zr_{58.5}Cu_{15.8}Ni_{12.5}Al_{10.3}Nd_{7.8}$	630	12.7	3.1
10	$(La_{0.7}Ce_{0.3})_{68}Al_{10}Cu_{20}Co_2$	366	12.9	3.1	33	$Dy_{55}Al_{25}Co_{20}$	632	12.8	3.1
11	$(La_{0.9}Ce_{0.1})_{68}Al_{10}Cu_{20}Co_2$	367	13.4	3.2	34	$Y_{55}Al_{25}Co_{20}$	638	12.7	3.1
12	$La_{68}Al_{10}Cu_{20}Co_2$	374	13.4	3.2	35	$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	640	12.9	3.1
13	$Ca_{65}Mg_{15}Zn_{20}$	375	13	3.1	36	$Pd_{77.5}Cu_6Si_{6.5}$	640	12.7	3.1
14	$Ce_{62}Al_{10}Cu_{20}Co_3Ni_5$	378	13.4	3.2	37	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	650	12.5	3.0
15	$Zn_{40}Mg_{11}Ca_{31}Yb_{18}$	400	13.2	3.2	38	$Ho_{55}Al_{25}Co_{20}$	651	12.6	3.0
16	$La_{62}Al_{14}Cu_{20}Ag_4$	404	13.4	3.2	39	$Zr_{65}Cu_{15}Ni_{10}Al_{10}$	652	12.8	3.1
17	$Mg_{65}Cu_{25}Tb_{10}$	413	13.5	3.2	40	$Zr_{55}Al_{10}Ni_5Cu_{30}$	682	12.8	3.1
18	$Mg_{65}Cu_{25}Sm_{10}$	416	13.2	3.2	41	$Zr_{55}Cu_{25}Ni_{10}Al_{10}$	685	13.3	3.2
19	$Mg_{65}Cu_{25}Gd_{10}$	417	13.3	3.2	42	$Cu_{46}Zr_{46}Al_7Gd_1$	700	12.9	3.1
20	$Mg_{65}Cu_{25}Ho_{10}$	417	12.6	3.0	43	$Cu_{46}Zr_{46}Al_8$	701	13.3	3.2
21	$Mg_{65}Cu_{25}Y_{10}$	418	12.9	3.1	44	$Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$	719	12.9	3.1
22	$La_{57.6}Al_{17.5}Cu_{12.4}Ni_{12.5}$	435	13.1	3.2	45	$Zr_{44}Cu_{44}Al_6Ag_6$	722	13.1	3.2
23	$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	455	12.8	3.1					

in liquids. It is clear that the value of C_V^{trans} is just $\frac{3}{2}R$ for one mole atoms in these liquid metals. Therefore, the result in Fig. 5 is a strong evidence to support our understanding of liquids and the glass transition. It is not necessary and useful to understand describe the heat capacity step at T_g with the dynamics of undercooled liquids.
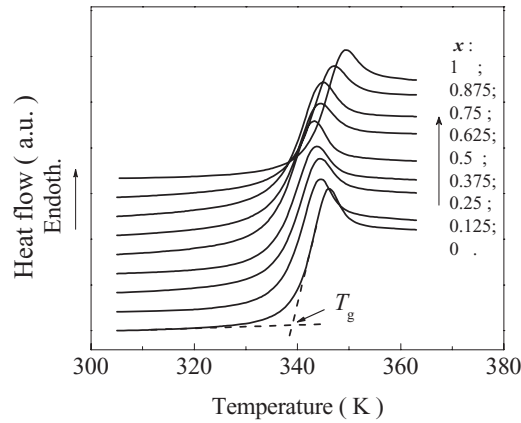
FIG. 6. DSC curves of $[x\text{NaNO}_3 (1\text{-}x)\text{KNO}_3]_{60} \cdot [\text{Ca(NO}_3)_2]_{40}$ ($0 \leq x \leq 1$) glassy samples measured during a heating at 20 K/min.

TABLE III. The compositions, glass transition temperature T_g, fragility index m and the jumps in heat capacity ΔC_p at T_g for $[x\text{NaNO}_3 \cdot (1\text{-}x)\text{KNO}_3]_{60} \cdot [\text{Ca(NO}_3)_2]_{40}$ ($0 \leq x \leq 1$) and $\text{Ca(NO}_3)_2 \cdot y\text{H}_2\text{O}$ ($y = 4\sim13$) glass-forming systems.

Ca(NO$_3$)$_2 \cdot y$H$_2$O			[xNaNO$_3 \cdot$ (1-x)KNO$_3$]$_{60} \cdot$ [Ca(NO$_3$)$_2$]$_{40}$			
y	T_g (K)	ΔC_p (J$\cdot$mol$^{-1}\cdot$K^{-1})	x	T_g (K)	m	ΔC_p(J$\cdot$mol$^{-1}\cdot$K^{-1})
4	212	234.3	0	339	105	65.5
5	202	281.3	0.125	336	91.5	63.6
6	194	295.5	0.25	335	83.7	66.5
7	187	358.5	0.375	335	80.5	63.8
8	182	397.5	0.5	334	66.7	64.4
9	178	434.3	0.625	335	87.1	65.6
10	174	477.5	0.75	335	94	63.3
11	171	504.2	0.875	337	102.5	65.4
12	168	534.8	1	341	104	65.8
13	166	570.2				

2. Heat capacity step at T_g for glass formers containing molecules

Glass formers containing molecules have wide spectra. Among them, the glass forming systems with the composition of $[x\text{NaNO}_3 \cdot (1\text{-}x)\text{KNO}_3]_{60} \cdot [\text{Ca(NO}_3)_2]_{40}$ ($0 \leq x \leq 1$) and $\text{Ca(NO}_3)_2 \cdot y\text{H}_2\text{O}$ ($4 \leq y \leq 13$) are simple, and offer a good opportunity to understand the heat capacity step at T_{g} for glass formers containing molecules. The glass formers contain simple molecules (NO_3^{-1} or/and H_2O molecules) and potassium, sodium and calcium ions. The metallic ions with spherical charge distributions can be considered as spherical particles, while nitrate ions with trigonal shape and H_2O molecules with rigid bent are typical simple no-spherical particles. So the former system is regarded as a binary mixture, while the latter is a simple ternary mixture.

Figure 6 shows the DSC curves for the $[x\text{NaNO}_3 \cdot (1\text{-}x)\text{KNO}_3]_{60}[\text{Ca(NO}_3)_2]_{40}$ ($0 \leq x \leq 1$) glass formers. All of curves were measured at a heating rate of 20 K/min. The measurements for each sample followed a cooling from the temperature ($T_g + 20$ K) at 20 K/min. The values of T_g determined by the usual way are found to depend on the composition. With the replacement of the first alkali ionic (K^+) by the second alkali ionic Na^+, T_g decreases gradually to a minimum as x approaches to 0.5. The phenomenon representing the alkali-mixed effect has been found in other systems.[62] The fragility index m of GFLs determined by DSC method,[63] T_g, and the heat capacity step ΔC_P at T_{g} for the system are listed in Table III. In Fig. 7, the composition dependence of the fragility index m and the ΔC_P of the $[x\text{NaNO}_3 (1\text{-}x)\text{KNO}_3]_{60} \cdot [\text{Ca(NO}_3)_2]_{40}$ system is exhibited. $[\text{KNO}_3]_{60}[\text{Ca(NO}_3)_2]_{40}$ with extreme $x = 0$ is termed usually as CKN, whose m is 107. As x tends to 0.5, m approaches to a minimum. In contrast, the ΔC_p is almost independent of the composition, and
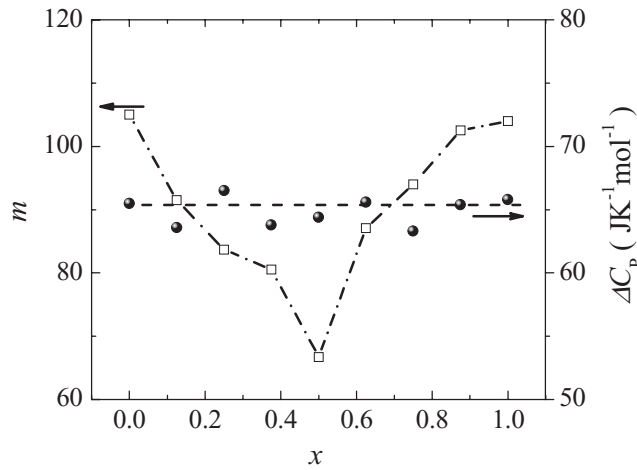
FIG. 7. x dependence of the ΔC_p at T_g and the fragility index m for $[xNaNO_3 \, (1\text{-}x)KNO_3]_{60} \cdot [Ca(NO_3)_2]_{40}$ glass-forming system.

close to 65.2 $JK^{-1} mol^{-1}$ within the experimental error of 5%. Obviously, it is difficult to explain the constant ΔC_p with the corresponding dynamic parameter m in the glass forming liquids. The reputed understanding that glass forming liquid (GFL) with large m has a large ΔC_p at T_g[21,61] means that the ΔC_p should vary with the composition in this GFL system.

The composition-independence of the ΔC_p in this binary system is consistent with our under-standing of liquid heat capacity. The ΔC_p must be related to some types of basic motions for the tiny particles. Clearly, the motions for the tiny particles exist in liquids and undercooled liquids, but the rigid glasses within the DSC probing time scale. With our understanding, the motions must be translational motions. The translational motions for different metallic ions (K^+, Na^+, and Ca^{2+}) are equivalent to contribute the liquid heat capacity. So it is found that the ΔC_p at T_g in the system is invariable as K^+ is replaced by Na^+. Obviously, the contribution of translational motions for NO_3^- atomic groups is different from the atomic contribution in this binary system since the former particles are non-spherical and the latter are spherical. Then, the ΔC_p is separated into two parts: cationic and anionic ones. Defining C_P^{ca} related to one molar cations and C_P^{an} for one molar anionic NO_3^-, the ΔC_p is the system is given by the form as: $\Delta C_P = C_P^{ca} + 1.4 \cdot C_P^{an} = 64.9 \, JK^{-1}mol^{-1}$. To confirm further the understanding of the origin of ΔC_p, it is necessary to deduce the values of the C_P^{ca} and C_P^{an} from the experimental results, where another equation containing the C_P^{ca} and C_P^{an} is necessary.

Figure 8 shows the DSC curves for a series of $Ca(NO_3)_2 \cdot yH_2O$ ($4 \leq y \leq 13$) samples. The values of T_g and the ΔC_p at T_g for all of materials are listed in Table III. In this system, T_g decreases gradually with the increasing H_2O content, while the ΔC_p at T_g increases. The large value of ΔC_p at T_g for $Ca(NO_3)_2 \cdot 4H_2O$ (about 234.3 $JK^{-1} mol^{-1}$) was explained qualitatively with its large m (~ 100).[64] However, one can find that the ΔC_p of $Ca(NO_3)_2 \cdot 4H_2O$ is much larger than the ΔC_p ($\sim 65 \, J \cdot K^{-1} \cdot mol^{-1}$) of CKN, while the m of $Ca(NO_3)_2 \cdot 4H_2O$ is smaller than that of CKN (107). According to our understanding, the obvious reason is that the number of the tiny particles in one molar $Ca(NO_3)_2 \cdot 4H_2O$ system is more than that in CKN system. Same as the above description of the ΔC_p at T_g in $[xNaNO_3 \, (1\text{-}x)KNO_3]_{60} \cdot [Ca(NO_3)_2]_{40}$ system, the ΔC_p for $Ca(NO_3)_2 \cdot yH_2O$ system is given as the form, $\Delta C_P = C_P^{ca} + 2 \cdot C_P^{an} + y \cdot C_P^{H_2O}$, where $C_P^{H_2O}$ is related to one molar H_2O molecules. It is clear that the only variable in the equation is H_2O molar content y. If this description can be applied well, it will be found that the change of ΔC_p in the system must be proportional to the change of y. Correspondingly, the values of the $C_P^{H_2O}$ and the sum $C_P^{ca} + 2 \cdot C_P^{an}$ can be deduced from the linear relation between the ΔC_p and y. The linear increase of the ΔC_p with the increase of y in the system is confirmed in the inset of Fig. 8. The slope and the intercept on
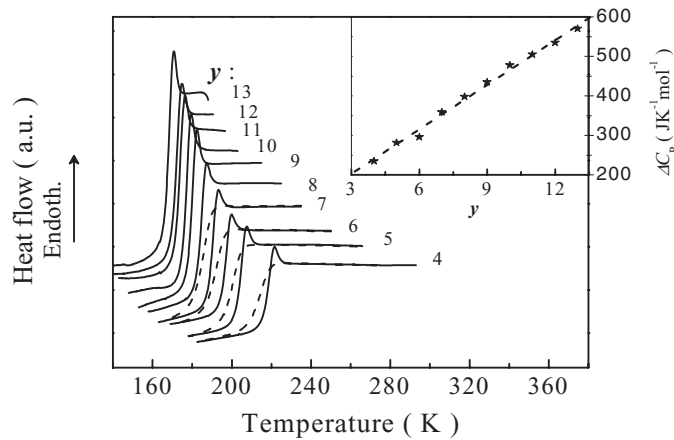
FIG. 8. DSC curves for series of $Ca(NO_3)_2 \cdot yH_2O$ ($4 \leq y \leq 13$) glassy samples measured during a heating at 20 K/min. The dash lines are the curves measured during a cooling at 10K/min. The inset displays the linear relation between ΔC_p at T_g and y in $Ca(NO_3)_2 \cdot yH_2O$ system. The slope of the fitting line is 37.8 J·mol^{-1} ·K^{-1}, and interact on vertical axis is 87.6 J·mol^{-1} ·K^{-1}.

vertical axis of the linear relation are 37.9 and 87.6 J·mol^{-1}·K^{-1}, respectively. Thus, the values of $C_P^{H_2O}$ and $C_P^{ca} + 2 \cdot C_P^{an}$ are deduced to 37.9 and 87.6 J·mol^{-1}·K^{-1}.

The combination of the two following functions, $C_P^{ca} + 1.4 \cdot C_P^{an} = 64.9\,\mathrm{JK^{-1}mol^{-1}}$ and $C_P^{ca} + 2 \cdot C_P^{an} = 87.6\,\mathrm{JK^{-1}mol^{-1}}$ makes it sure to deduce the values of the C_P^{ca} and C_P^{an}. The resultant values are 12.0 and 37.8 J·mol^{-1}·K^{-1} for the C_P^{ca} and C_P^{an}. With a certain approximation, the values of the C_P^{ca}, C_P^{an} and $C_P^{H_2O}$ can be written into the form as follows, $C_P^{ca} = \frac{3}{2}R$ (approximately 12.5 J·mol^{-1}·K^{-1}), $C_P^{an} \cong C_P^{H_2O} \cong \frac{9}{2}R$ ($\sim$ 37.4 J·mol^{-1}·K^{-1}). The values of the C_P^{ca}, C_P^{an} and $C_P^{H_2O}$ give a strong evidence to support our understanding of the glass transition since a definitive physical meaning can be offered to these values of the C_P^{ca}, C_P^{an} and $C_P^{H_2O}$. It is not coincidental that the C_P^{ca} is exactly equal to the ΔC_P at T_g in bulk metallic GFLs. In nature, both of them correspond to the atomic translational motion. The atomic translational motion contribution to heat capacity is just $\frac{3}{2}R$ per molar atoms. One NO_3^- molecule in space, a planar triangle, has two rotational degrees of freedom. Besides the two rotational degrees of the planar triangle, the NO_3^- molecule, owning to its resonance structure, has another rotational degree of freedom. This freedom is related to the rotation of three oxygen atoms around the central nitrogen atom. According to our model of liquid heat capacity, there are three molecular forms to move translationally in total for one NO_3^- atomic group in the liquid. Correspondingly, the heat capacity contribution arising from NO_3^- molecular translational motions in liquid state is $\frac{9}{2}R$ per molar molecules. Same absolutely as the molecule in water, one H_2O molecule, regarded as a rigid bent, has three degrees of rotational freedom in $Ca(NO_3)_2 \cdot yH_2O$ glass forming liquids. Then one H_2O molecule has three molecular forms to move translationally in liquid. The heat capacity contribution of one mole H_2O molecular translational motion is equal to $\frac{9}{2}R$. Therefore, the values of the C_P^{ca}, C_P^{an} and $C_P^{H_2O}$ are exactly equal to their translational contribution to heat capacity in liquids. The results support further that the origin of the glass transition in the two glass former systems is the falling out-of-equilibrium of all of transitional motions in their liquids.

3. Heat capacity step related to the "bead" idea

Wunderlich[65] has analyzed the excess heat capacity ΔC_P relative to the corresponding glass at T_g for 41 monomeric and polymeric glass formers, and proposed firstly that the ΔC_P could be understood with the term of "bead". Due to that the thermal energy (corresponding to temperature) can excite mutual arrangement of atomic groups of different sizes (e.g., –CH–, –CH=CH–, –NH2, and so forth) without destroying or decomposing the whole organic molecule, it is useful to introduce the idea of a bead in organic liquids. The bead is defined as any tightly bound atomic group that

serves as a quasi-independent unit in the molecular structure. The "per-bead basis" idea has been found suitably for comparisons of the excess heat capacity ΔC_P at T_g in polymeric glass formers. It has been shown to be associated with an approximately constant contribution of around 11.3 JK^{-1} per molar beads to the ΔC_P. The bead contribution to ΔC_P was understood qualitatively by Erying's hole model of liquids.[66] On a molecular level, it is necessary for a rearrangement of neighboring molecules or molecule segments to allow the creation or disappearance of a hole. The contribution of the creation new holes on heat capacity is proportional to the change of the number of holes with temperature. This intuitive explanation is lack of physical meaning since holes or volume related to molecule or molecular segments in liquids can not be defined rigidly. In theory or experiment, it is not really possible to test any molecular and its segmental volume mathematical expression of heat capacity. There is a more serious problem. Within the per-bead basis idea, the ΔC_P for glass formers is close to a constant. Accumulated experimental results are not consistent with this idea.

According to our understanding, a clear picture can be given to the physical meaning of the contribution of beads. Obviously, the bead idea is useful for atomic systems (e.g. the above metallic glass forming liquids) where all atoms in the system are susceptible to thermal activation. Atomic translational motion with statistical equilibrium in liquid state is the origin of the excess heat capacity of liquids relative to their ideal rigid solids. The ΔC_P in atomic liquid system is equal to atomic translational contribution, C_V^{trans}, whose value is $\frac{3}{2}R$ (12.5 JK^{-1}) per molar atoms. With the term of bead, the bead contribution in atomic glass forming liquids is $\frac{3}{2}R$ (11.3 JK^{-1}) per molar beads, and is consistent with the constant contribution found by Wunderlich. In most polymeric glass forming liquids, the rotation of any polymeric molecule may be different from that of the simple molecules, e.g., H_2O molecule and NO_3^- atomic group. It is too difficult to be activated by thermal energy because of its complex molecular fine structure (e.g., considerable length). Since the liquid feature that is unable to bear any shear still exists for these liquids, it is appropriate to think that any polymeric molecule as a whole can be activated thermally to move translationally from its position to a new neighboring one. Without the rotational effect, the number of the molecular forms to move translationally is determined mainly by the flinging of the different segments insider the molecules. The flinging of one molecular segment will add one molecular form to the whole molecular translational motion. The corresponding translational contribution arising from one adding molecular form is $3R/2$ per one mole molecules. The glass transition is the falling out-of-equilibrium of the translational motion in liquids. Correspondingly, with the term of "bead" the excess heat capacity ΔC_P at T_g in polymeric glass formers is an approximately constant of around $3R/2$ per molar beads.

In practice, it has found that a relatively constant of ΔC_P could not be yielded for glass forming liquids with wide spectra. In the above analysis, there is a pre-condition to yield the constant of $3R/2$ per molar beads at T_g for molecular liquids. That is, the molecule as a whole has not rotational motions in liquids. In fact, usual molecules in most molecular liquids can be activated to rotate in space, e.g., H_2O and NO_3^{-1} molecules. With the term of "bead", H_2O and NO_3^{-1} beads will contribute $9R/2$ to the ΔC_P at T_g, but $3R/2$. Therefore, even though bead idea is useful in general to compare the ΔC_P at T_g for glass forming liquids with wide spectra, it is too rude to conclude that bead contribution is constant of $3R/2$ to the ΔC_P at T_g. In order to clarify the intrinsic origin of the contribution of bead with our understanding, o-terphenyl OTP) molecular liquid,[67] a typical molecular glass forming liquid with a good glass forming ability, is offered. It is known that one OTP molecule consists of a central benzene ring and two lateral phenyl rings in *ortho* position.[68] For this glass former, the ΔC_p relative to rigid glass is 112 JK^{-1} mol^{-1} at T_g (246 K).[69] Different from most complex polymeric molecules, any OTP molecule as a whole in liquid state can rotate in equilibrium. At the same time, the two lateral phenyl benzene rings rotate as well. The combination of the rotations of whole molecule and lateral benzene rings figure out the number of OTP molecular forms to move translationally is nine. That is, there are three molecular forms to rotate for the molecule as a whole because of the rotation of the lateral benzene rings. The number of rotational degrees of freedom for OTP molecule as a whole is three also. Therefore, the contribution of OTP molecular translational motions to heat capacity is $27R/2$ per molar molecules, whose value is 112 JK^{-1} mol^{-1}. This further supports our understanding on the glass transition. The falling out-of-equilibrium of the transitional motions is the nature of the glass transition in OTP glass former.

V. SUMMARY AND OUTLOOK

As the task of a model of liquids that to make it possible to understand and predict the properties of liquids, we adopt the purist view starting from information that a liquid matter is composed up of tiny particles (e.g. atoms or molecules or atoms and molecules). We are inclined to care about the universal existence of the interactions among the tiny particles, leaving their complex and detailed responsibilities. All of these simplifications make it possible to simplify the varying situations of different tiny particles in liquid state into one universal pattern: Any tiny particle is posited with a certain potential energy well. Contrary to what is often stated, the complicated interactions in liquids represent the properties of liquids, we manage to connect basic liquid features with the motions of the tiny particles accompanying with the potential energy well. The basic motions of the tiny particles limited in the potential energy well involve vibration and rotation. The later motion exists only for no-spherical particles. Different from rigid solids, liquids contain translational motions of their tiny particles that need to overcome an energy barrier related to the potential energy well. Moreover, owing to high thermal energy (corresponding the higher temperature liquid region), the translational motions in statistical equilibrium exist in liquid. This is the origin of liquid that has inability to bear any shear.

According to the liquid model, heat capacity of simple liquids that contain common features of numerous real liquids is proposed. Considering that heat capacity of liquids represents the motions of their tiny particles in statistical equilibrium and the thermal effect of inner motions insider tiny particles is too weak to take into account, we separate the liquid heat capacity into three parts: the contribution C_V^{vib} arisen from vibrations, the C_V^{rot} from rotations and the C_V^{tran} from transitional motions. The descriptions of C_V^{vib} and C_V^{rot} are same as those in solids and gases, and are well described in statistical physics textbook. During to the high temperature corresponding to liquid region, the C_V^{vib} and the C_V^{rot} are of temperature-independence, and equal to $3R$ and $\frac{i}{2}R$ per molar tiny particles. The value of i is the number of the degrees of rotational freedom. For spherical tiny particles, its C_V^{rot} does not exist. The value of C_V^{tran} is also independence of temperature, and equal to $\frac{3i}{2}R$, where i is the number of the forms of tiny particle. For liquids containing simple molecules, the value of i is determined by the number of rotational degrees of freedom. For liquids containing complex molecules, the value of i is not only determined by the number of rotational degrees of freedom, but also the rotations and flinging of inner molecular segments.

The models of simple liquids and their heat capacity are useful to understand the glass transition. On the view of statistical physics, no intrinsic difference between normal liquids and their undercooled liquids. Within the normal experimental time scale, translational motions are statistical equilibrium in both normal and undercooled liquids. It is found that the heat capacity step across the glass transition is equal exactly to the C_V^{tran}. This finding gives a strong and direct evidence to support that the glass transition is the falling out-of-equilibrium of the translational motions in liquids.

It is too early to tell whether or not the models of liquids and their heat capacity give the basically correct explanation of the thermodynamic properties of liquids. Importantly, the complex dynamic behaviors of liquids are not involved in details yet, even though a few experimental results on the dynamics support the models. If this is the case, there are several notable conclusions:

- Liquids are the condensed matter with disorder microstructure, where translational motions are in statistical equilibrium at the probing time scale.
- Heat capacity of liquids with statistical equilibrium state is equal to the additions of the contributions arising from all motions of the tiny particles (atoms and molecules).
- No intrinsic difference exists between normal liquids (above T_m) and undercooled liquids (below T_m).
- The glass transition in liquids is the falling out-of-equilibrium of all translational motions in liquids.
- The excess heat capacity step across the glass transition is determined by the translational motions in liquids. This makes it easier to predict and confirm the basic characteristics accompanied by the glass transition in glass forming liquids.

For a number of reasons the study of liquids and the undercooled liquids approaching the glass transition is likely to remain an exciting branch of condense-matter physics for years to come. One reason is that the physics and chemistry of the tiny particles composing liquids, especially the complex molecules with large molecular size and many molecular segments, are unsolved. This lacking makes the quantitative description of the thermodynamic properties of most real liquids impossible. The second reason is that it is considerably simple to assume the energy barrier with the potential energy well for all of tiny particles to move translationally in liquids relative to thermal energy k_BT is not high and the translational motions of all of tiny particles are in statistical equilibrium. If the energy barriers for some tiny particles, compared with k_BT, are so high that the translational motions of these particles is not in statistical equilibrium, the disordered condensed matter systems will be in the state of partial equilibrium. These systems, partially liquids-like, have not been involved in details here yet. The third reason is that the effect of the molecular rotation and inner rotation on the number of molecular form to move translationally is still lack of rigid theoretical calculations, even though it is intuitive and reasonable with the basic principles in the statistical physics. Importantly, computers are still too slow for the secrets of undercooled liquid to be revealed by brute simulations. Fourth reason is that the glass transition involves not only thermodynamic properties of liquids, but also the complex dynamic behaviors of liquids. The clarification of the complex dynamic behaviors with the translational motions in liquids has not been carried out. Therefore, the research field in liquids and the glass transition is still open to new theoretical developments and phenomenological modeling. Future breakthroughs are likely to take place from more careful and accurate experimental efforts.

[1] T. Iidea and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon press, Oxford, 1988).
[2] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[3] F. N. Keutsch and R. J. Saykally, PNAS **98**, 10533 (2001).
[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Beijing World Publishing Corporation by arrangement with Butterworth-Heineman, 1999).
[5] J. Frenkel, *Kinetic Theory of Liquids*, edited by R. H. Fowler, P. Kapitza, and N. F. Mott (Oxford University Press, 1947), p. 188.
[6] J. M. Ziman, *Models of disorder* (Cambridge University Press, 1979).
[7] J. P. Hansen and I. R. McDonald, *Theory of simple liquids* (Elsevier, 2007).
[8] E. Donth, *The Glass Transition: Relaxation Dynamics in liquids and Disordered Materials* (Soringer-Verlag Berlin Herdelber, 2001).
[9] J. Jäckle, Rep. Prog. Phys. **49**, 171 (1986).
[10] J. C. Dyre, Rev. Mod. Phys. **78**, 953 (2006).
[11] P. G. Debenedetti and F. H. Stillinger, Nature **410**, 259 (2001).
[12] J. C. Dyre, N. B. Olse, and T. Christensen, Phys. Rev. B **53**, 2171 (1996).
[13] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[14] S. P. Das, Rep. Prog. Phys. **76**, 785 (2004).
[15] M. H. Cohen and D. J. Turnbull, Chem. Phys. **31**, 1164 (1959).
[16] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[17] O. Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, and T. Matsuo, J. Phys. Chem. B **102**, 1605 (1998).
[18] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).
[19] X. Xia and P. G. Wolynes, PNAS **97**, 2990 (2000).
[20] H. Tanaka, Phys. Rev. Lett. **90**, 055701 (2003).
[21] C. A. Angell, in *Relaxationsin Complex Systems*, edited by K. L. Ngai and G. B. Wright (U.S. GPO, Washington, DC), p. 3.
[22] H. B. Ke, P. Wen, and W. H. Wang, arXiv:1111.4826v1; arXiv:1111.4608v1; arXiv:1107.1921v1.
[23] H. B. Ke, Z. F. Zhao, P. Wen, and W. H. Wang, Chin. Phys. Lett. **29**, 046402 (2012).
[24] H. B. Ke, P. Wen, and W. H. Wang, Sci. in China Series G: Physics, Mechanics and Astronomy (to be published).
[25] H. B. Ke, in the PhD thesis, CAS (2012).
[26] B. Chen, J. Xing, and J. I. Siepmann, J. Phys. Chem. **104**, 2391 (2000).
[27] E. W. Kellermann, Prog. Roy. Soc. A **178**, 17 (1941).
[28] E. O. Wollan, W. L. Davidson, and C. G. Shull, Phys. Rev. **75**, 1348 (1949).
[29] J. Liu, C. G. Duan, M. M. Ossowski, W. N. Mei, R. W. Smith, and J. R. Hardy, Phys. Chem. Minericals **28**, 258 (2001).

[30] S. H. Chen, J. Teixeira, and R. Nicklow, Phys. Rev. A **26**, 3477 (1982).

[31] J. Teixeira, M.-C. Bellissent-Funel, S. H. Chen, and A. J. Dianoux, Phys. Rev. A **31**, 1913 (1985).

[32] C. J. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoff, and P. L. Geissler, Science **301**, 1698 (2003).

[33] M. T. Cicerone, and M. D. Ediger, J. Chem. Phys. **104**, 7210 (1996).

[34] D. V. Schroeder, *An Introduction to Thermal Physics* (Addison Wesley Longman, 2000).

[35] R. Bellissent and G. Tourand, J. Non-Cryst. Solids **35**, 1221 (1980).

[36] B. Castaing and J. Souletie, J. Phys. I **1**, 403 (1991).

[37] C. Monthus and J. Bouchaud, J. Phys. A **29**, 3847 (1996).

[38] R. Kohlrausch, Ann. Phys. Chem. (Leipzig) **91**, 179 (1874); G. Willians and D. C. Watts, Trans, Faraday Soc. **66**, 80 (1970).

[39] H. Sillescu, J. Non-Cryst. Solids **243**, 81 (1999).

[40] O. Kubaschewski and C. B. Alcock, *Metallurgical thermochemistry* (5th Edn, revised and enlarged), (Pergamon Press, Oxford, 1979), p. 336.

[41] A. Einstein, Ann. Phys., Lpz. **22**, 180; 800 (1907).

[42] P. Debye, Ann. Phys., Lpz. **39**, 789 (1912).

[43] National Institute of Standards and Technology database.

[44] W. F. Giauque and J. W. Stout, J. Am. Chem. Soc. **58**, 1144 (1936).

[45] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, J. Chem. Phys. **33**, 1751 (1960).

[46] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Res. Natl. Bur. Stand. **23**, 197 (1939).

[47] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, 1976).

[48] J. B. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).

[49] A. Zajac, J. Chem. Phys. **29**, 1324 (1958).

[50] E. O. Wollan, W. L. Davidson, and C. G. Shull, Phys. Rev. **75**, 1348 (1949).

[51] R. C. Dougherty and L. N. Howard, J. Chem. Phys. **109**, 7379 (1998).

[52] Considering the O-H bond length in H_2O molecule is 0.9584 Å and the H-O-H bond angel is 104.5°, the moment of inertia I_{xx}, I_{yy}, and I_{zz} for H_2O molecule are 1.09×10^{-47}, 1.91×10^{-47} and 3.0×10^{-47} kgm^2, respectively.

[53] A. L. Greer, Science **267**, 1947 (1995).

[54] P. Wen, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. P. Huang, and M. L. Guo, Appl. Phys. Lett. **84**, 2790 (2004).

[55] Z. F. Zhao, P. Wen, C. H. Shek, and W. H. Wang, Phys. Rev. B **75**, 174201 (2007).

[56] A. Meye, R. Busch, and H. Schober, Phys. Rev. Lett. **83**, 5027 (1999).

[57] X. P. Tang, U. Geyer, R. Busch, W. L. Johnson, and Y. Wu, Nature **402**, 160 (1999).

[58] N. Nishiyama, M. Horino, O. Haruyama, and A. Inoue, Appl. Phys. Lett. **76**, 3914 (2000).

[59] D. Xu and W. L. Johnson, Phys. Rev. B **74**, 024207 (2006).

[60] H. B. Ke, P. Wen, D. Q. Zhao, and W. H. Wang, Appl. Phys. Lett. **96**, 251902 (2010).

[61] D. Huang and G. B. McKenna, J. Chem. Phys. **114**, 5621 (2001).

[62] T. Komatsu and T. Noguchi, J. Am. Ceram. Soc. **80**, 1327 (1997).

[63] P. Wen, P. Harrowell, and C. A. Angell, J. Phys. Chem A **115**, 6260 (2011).

[64] L. M. Wang, C. A. Angell, and R. Richert, J. Chem. Phys. **125**, 074505 (2006).

[65] B. Wunderlich, J. Phys. Chem. **64**, 1052 (1960).

[66] N. Hirai and H. Eyring, J. Appl. Phys. **29**, 810 (1958).

[67] A. Tölle, Rep. Prog. Phys. **64**, 1473 (2001).

[68] I. L. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 1974 (1944).

[69] S. S. Chang and A. B. Bestul, J. Chem. Phys. **56**, 503 (1972).