Letters

Foundation of the Adam–Gibbs Relation

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On the basis of the free energy landscape (FEL) approach to non-equilibrium systems, the cooperatively rearranging region (CRR) is defined as a region in the FEL which supports two basins and the entire configurational space is tessellated by a set of CRR's. The configurational entropy is shown to be in proportion to the inverse of the average size of CRR. The average rate of structural relaxation defined by a geometrical mean of the transition rate in each CRR is shown to be written in the form of the Adam–Gibbs relation. Various estimations of the size of CRR reported before are assessed on the basis of the proper definition of CRR and the configurational entropy.

Structural relaxation in non-equilibrium systems plays an essential role in determining their properties.[1,2] There has been a belief that an elementary process of the structural relaxation occurs in a cooperatively rearranging region (CRR) which was proposed by Adam and Gibbs.[3] The Adam–Gibbs relation states that the relaxation rate $W(T)$ at temperature T is related to a configurational entropy $S_C(T)$ through

$$W(T) = w_0 \exp\left(-\frac{\mathcal{A}}{TS_C(T)}\right), \quad (1)$$

where $\mathcal{A}$ is a positive constant and w_0 is an attempt frequency. Their argument is based on two assumptions: one is that the rate of structural relaxation is essentially determined by the smallest CRR z^* and is given by

$$W(T) = w_0 \exp\left(-\frac{z^* \Delta \mu}{k_B T}\right), \quad (2)$$

where $\Delta \mu$ is the activation free energy per molecule and k_B is the Boltzmann constant. The other is that the configurational entropy s_C^* of CRR of size z^* is given by

$$s_C^* = z^* S_C / N \quad (3)$$

because of the extensivity of entropy, and the configurational entropy $S_C(T)$ is given by the configurational partition function determined by the potential energy and the volume.

The Adam–Gibbs relation (1) has been used most frequently in the analysis of relaxation in non-equilibrium systems, since it relates a dynamic quantity to a thermodynamic quantity. For example, the Adam–Gibbs relation has been exploited in a theoretical analysis of glass transition.[4] However, there is a theoretical argument which disagrees with the reasoning by Adam and Gibbs in the dimensionality dependence of correlation length.[5]

Since assumptions in the argument of Adam and Gibbs are sloppy and ambiguous, there have been many different interpretations of CRR and experiments have been reported to determine the size of the CRR based on different interpretations. Yamamuro et al.[6,7] have obtained the configurational entropy by subtracting the kinetic contribution from the entropy which are computed from the specific heat. Using Eq. (3), they reported the size z^* of CRR for various materials at their glass transition temperature T_g which are less than 10 molecules.

Some researchers considered that the CRR is the area of fluctuation of thermodynamic quantities,[8,9] and other researchers regarded it as the area of dynamic heterogeneity which can be determined by photo-probe experiments[10,11] and by combining quasi-elastic neutron scattering and positron annihilation life time spectroscopy.[12] According to these experiments, the size of CRR is estimated to be more than 100 molecules.

On the theoretical side, an idea of random first order transition (RFOT) has been proposed[13,14] and many researches have been reported to explain the glass transition on the basis of the RFOT theory. The basic idea is to regard the supercooled liquid state as a mosaic of entropic droplets which are considered to correspond to the CRR since the dependence of the viscosity on the configurational entropy is the same as the Adam–Gibbs expression.[15] In this approach, the configurational entropy is defined by a similar argument to the Adam and Gibbs argument.

Key questions at this moment are what are the proper definitions of the CRR and the configurational entropy, and if the Adam–Gibbs relation (1) still holds with these proper definitions. In this letter, I give an answer to these key questions on the basis of the free energy landscape (FEL) approach to non-equilibrium statistical mechanics[16] and present a foundation of the Adam–Gibbs relation. I also assess various interpretations of CRR.

I begin with a proper definition of the configurational entropy. In the statistical mechanics based on the FEL approach, an N body distribution function $\rho_N(\{r_i\}; \{R_i\})$ is introduced which is determined by fast motion of each atom around its average position $\{R_i\}$, and the partition function is written as

$$Z(T, V, N) = \frac{1}{N!} \int Z(T, V, N, \{R_i\}) \, d\{R_i\}, \quad (4)$$

where the partial partition function $Z(T, V, N, \{R_i\})$ is defined by

$$Z(T, V, N, \{R_i\}) = \frac{1}{h^{3N}} \int \exp\left[-\frac{H(\{r_i\}, \{p_i\})}{k_B T}\right]$$
$$\times \rho_N(\{r_i\}; \{R_i\}) \, d\{r_i\} \, d\{p_i\}. \quad (5)$$

Here, T, V, and N are the temperature, volume and number of atoms, respectively, and h is the Planck constant and $H(\{r_i\}, \{p_i\})$ is the Hamiltonian, where $\{r_i\}$ and $\{p_i\}$ are the position and momentum of i-th atom. The probability distribution function $P(\{R_i\})$ of a configuration $\{R_i\}$ is given by[16]

$$P(\{\mathbf{R}_i\}) = \exp\left(-\frac{\Phi(\{\mathbf{R}_i\}) - F}{k_B T}\right). \qquad (6)$$

Here, $\Phi(\{\mathbf{R}_i\})$ is the FEL determined by the partial partition function

$$\Phi(T, V, N, \{\mathbf{R}_i\}) = -k_B T \ln Z(T, V, N, \{\mathbf{R}_i\}) \qquad (7)$$

and F is the free energy of the system

$$F = -k_B T \ln Z(T, V, N). \qquad (8)$$

Since the entropy is given by the temperature derivative of the free energy $S = k_B \partial[T \ln Z]/\partial T$, it can be written as[17]

$$S = \langle S(\{\mathbf{R}_i\})\rangle + \langle -k_B \ln P_{eq}(\{\mathbf{R}_i\})\rangle, \qquad (9)$$

where $S(\{\mathbf{R}_i\}) = k_B \partial[T \ln Z(T, V, N, \{\mathbf{R}_i\})]/\partial T$ is the entropy of configuration $\{\mathbf{R}_i\}$, and $\langle\cdots\rangle$ denotes an average over the probability distribution function $\langle\cdots\rangle = \int \cdots P(\{\mathbf{R}_i\}) \, d\{\mathbf{R}_i\}$.

The first term on the right hand side of Eq. (9) may be called the glass entropy and the second term is the configurational entropy S_C, namely

$$S_C = \langle -k_B \ln P(\{\mathbf{R}_i\})\rangle. \qquad (10)$$

This definition is different from that assumed by Adam and Gibbs[3] and by Kirkpatrick and Thirumalai.[5] The configurational entropy defined by Adam and Gibbs contains a part of glass entropy and thus it is larger than the proper configurational entropy. The definition of configurational entropy employed in Ref. 5 is the special case of Eq. (10), where only the configurations at local minima are considered and each minimum is assumed to be equally probable. Namely, if there are N_b equally probable basins, $P(\{\mathbf{R}_i\}) \cong 1/N_b$ and thus $S_C \cong k_B \ln N_b$. It is important to note the definition (10) of the configurational entropy is different from that of the Adam–Gibbs argument[3] which is related to the partition function due to the potential energy.

Next, I consider a relevant definition of CRR on the basis of the FEL approach. The FEL consists of many basins in the $3N$ dimension configurational space. Here, I assume monoatomic molecules for the sake of simplicity. It is straightforward to extend the present argument to polyatomic molecules. The FEL can be tessellated into a set of basins in the same spirit for the potential energy landscape.[18] The elementary process of structural relaxation is a transition from a basin to its adjacent basin. In order to keep the simple relation between the elementary process and the rearranging region, I define a CRR by the area of molecules forming two adjacent basins and tessellate the entire FEL into a set of CRR's as schematically shown in Fig. 1. I denote the k-th CRR as $\{\mathbf{R}_i\}_k$, the number of molecules in the k-th CRR as N_k and the probability of the CRR as $P_k(\{\mathbf{R}_i\}_k)$. The average size $\langle N_{CRR}\rangle$ of CRR is given by

$$\langle N_{CRR}\rangle = \frac{1}{L}\sum_{k=1}^{L} N_k = \frac{N}{L}, \qquad (11)$$

where L is the number of CRR's in the system.

Since $P(\{\mathbf{R}_i\}) = \prod_{k=1}^{L} P_k(\{\mathbf{R}_i\}_k)$, the configurational entropy Eq. (10) is given by

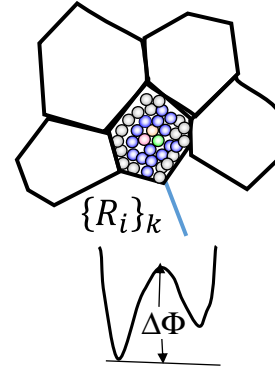$$S_C = \sum_{k=1}^{L} \langle -k_B \ln P_k(\{\mathbf{R}_i\}_k)\rangle = L s_C^*, \qquad (12)$$

Fig. 1. (Color online) A schematic view of tessellation of the configurational space into CRR's, where each CRR supports two adjacent local minima of the FEL.

where $s_C^* = \langle -k_B \ln P_k(\{\mathbf{R}_i\}_k)\rangle$ is the average configurational entropy of a CRR. Therefore, the average size $\langle N_{CRR}\rangle$ of CRR can be expressed as

$$\langle N_{CRR}\rangle = \frac{N s_C^*}{S_C}. \qquad (13)$$

If the configuration is represented by two minima, then $s_C^* = \langle -k_B\{p_k \ln p_k + (1 - p_k)\ln(1 - p_k)\}\rangle$, where p_k is the probability of one of two basins in the k-th CRR. When two minima are equally probable, $p_k = 1/2$ and $s_C^* = k_B \ln 2$.

Now, I move on to the discussion of relaxation rate. It is natural to assume that the transition rate $W_k(T)$ of the structural relaxation within the k-th CRR is given by

$$W_k(T) = w_0 \exp\left(-\frac{N_k \Delta\mu}{k_B T}\right), \qquad (14)$$

where $\Delta\mu$ is an activation free energy per molecule as in Eq. (2). Assuming that the transition within each CRR is independent, I define the transition rate of the structural relaxation $W(T)$ by a geometrical mean of $W_k(T)$

$$W(T) = \left(\prod_{k=1}^{L} W_k(T)\right)^{1/L}. \qquad (15)$$

It is straightforward to show that

$$W(T) = w_0 \exp\left(-\frac{\dfrac{1}{L}\sum_{k=1}^{L} N_k \Delta\mu}{k_B T}\right)$$

$$= w_0 \exp\left(-\frac{\langle N_{CRR}\rangle \Delta\mu}{k_B T}\right). \qquad (16)$$

Therefore, using Eq. (13), I obtain the Adam–Gibbs relation

$$W(T) = w_0 \exp\left(-\frac{\mathcal{A}}{T S_C(T)}\right) \qquad (17)$$

with $\mathcal{A} = \frac{\Delta\mu s_C^* N}{k_B}$. This completes the derivation of the Adam–Gibbs relation on the basis of the FEL approach.

Exploiting the present argument, I assess various experimental approaches to determine the size of CRR.

The definition of the CRR described above implies immediately existence of a group of atoms which change their positions within a CRR. I call these small number of molecules a simultaneously rearranging region (SRR), which

is smaller than the CRR. In fact, existence of such region has been proposed by Matsuoka and Quan[19] as conformers which relax together. They estimated that a typical size of the domain is 7–10 conformers at T_g.

There have been many researchers who considered the CRR as a sort of fluctuating area. Donth[8] considered the CRR as an area of thermodynamic fluctuation and estimated the size of CRR to be between 35 and 290 molecules on the basis of thermograms and formulas from a fluctuation theory of glass transition. Correlation of this kind of area with the fragility has been discussed by Bouthegrourd et al.[9] Observing dynamical quantities, some researchers regarded the CRR as an area of dynamical heterogeneity. Ediger et al.[10,11] observed a strong correlation between translational and rotational diffusion which was qualitatively explained by spatially heterogeneous dynamics. Kanaya et al.[12] considered that a CRR is the dynamically heterogeneous region. They obtained a void size by the positron annihilation lifetime spectroscopy and the mean square displacement by the quasielastic neutron scattering, and estimated the size of CRR by combining these results, and reported 113 molecules as the size of CRR of cis-1,4-polybutadiene at its T_g.

In the FEL approach, fluctuating or heterogeneous area is represented by local fluctuation of the structure of the FEL. The area of frequent motion corresponds to an area with shallow basins in the FEL, and thus the size of this area is supposed to be much larger than the size of CRR defined in the present approach. Estimations of the size of CRR from fluctuating areas overestimate the size of CRR and the smallest within the estimations may correspond to the proper size of CRR.

Yamamuro et al.[6,7] estimated the configurational entropy from the measurement of the specific heat and calculated z^* from Eq. (3). They reported 3.8 molecules for 3 bromopentane, 5.8 molecules for ethylbenzene and 6.7 molecules for Toluene for z^* at their T_g. Apparently, they have overestimated the configurational entropy due to misplacement of a part of glass entropy into the configurational entropy. It is also important to note that the estimation of entropy by integrating the specific heat needs some care. In fact, it is shown[17] that the specific heat is written as

$$C = C_g + C_c + \Delta C, \tag{18}$$

where $C_g = \langle T \partial S(\{\mathbf{R}_i\})/\partial T \rangle$ is the glass specific heat, $C_C = \langle \Delta \Phi(\{\mathbf{R}_i\}) \Delta E(\{\mathbf{R}_i\}) \rangle / k_B T^2$ is the configurational specific heat and $\Delta C = \langle \Delta S(\{\mathbf{R}_i\}) \Delta E(\{\mathbf{R}_i\}) \rangle / k_B T$ is the specific heat due to the temperature dependence of the probability distribution $P(\{\mathbf{R}_i\})$. Here, $\Delta A(\{\mathbf{R}_i\}) = A(\{\mathbf{R}_i\}) - \langle A(\{\mathbf{R}_i\}) \rangle$ for a physical quantity $A(\{\mathbf{R}_i\})$ of configuration

$\{\mathbf{R}_i\}$. This indicates that $S - \int C_g/T \, dT$ is larger than S_C.[16] Therefore, this difference also makes the estimation of the size of CRR smaller than the real size. If the configurational entropy is obtained correctly, then this method will give the proper size of CRR.

In the recent interpretation of the random first-order transition theory,[15] the length scale of an entropic droplet is supposed to be determined by balance between the free-energy gain due to configurational entropy and the surface energy. Although the derived relation between the viscosity and the configurational entropy coincides with the Adam–Gibbs expression, it is not clear if the length scale is identical to the size of a CRR.

In conclusion, the physically proper definition of CRR and the configurational entropy gives rise to the Adam–Gibbs relation, which in turn provides a strong support for the unified explanation of the glass transition singularities based on the FEL approach.[4,16] It is highly expected to determine the size of CRR by experiments and computer simulation on the basis of the present definition.

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