Theoretical study on density of microscopic states in configuration space via Random Matrix

Koretaka Yuge, Kazuhiro Takeuchi and Tetuya Kishimoto

Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

In classical systems, our recent theoretical study provides new insight into how spatial constraint on the system connects with macroscopic properties, which lead to universal representation of equilibrium macroscopic physical property and structure in disordered states. These important characteristics rely on the fact that statistical interdependence for density of microscopic states (DOMS) in configuration space appears numerically vanished at thermodynamic limit for a wide class of spatial constraints, while such behavior of the DOMS is not quantitatively well-understood so far. The present study theoretically address this problem based on the Random Matrix with Gaussian Orthogonal Ensemble, where corresponding statistical independence is mathematically guaranteed. Using the generalized Ising model, we confirm that lower-order moment of density of eigenstates (DOE) of covariance matrix of DOMS shows asymptotic behavior to those for Random Matrix with increase of system size. This result supports our developed theoretical approach, where equilibrium macroscopic property in disordered states can be decomposed into individual contribution from each generalized coordinate with the sufficiently high number of constituents in the given system, leading to representing equilibrium macroscopic properties by a few special microscopic states.

I. INTRODUCTION

In classical systems, statistical thermodynamics tells that macroscopic physical property (or macroscopic structure) in equilibrium state can be typically obtained by canonical average of $\mathcal{C} = Z^{-1} \sum_d C^{(d)} \exp \left( -\frac{E^{(d)}}{k_B T} \right)$, where $Z$ denotes partition function, $T$ is temperature, $d$ means possible microscopic state on phase space, and $E^{(d)}$ and $C^{(d)}$ are energy and physical property (or structure) in state $d$, respectively. When $T$ goes to zero, summation is performed for the ground states having lowest energy. When $T$ increases, due mainly to entropy contribution, the system can go into disordered states (e.g., states above the critical temperature). In the disordered states, direct determination of $\mathcal{C}$ through the definition of canonical average is practically intractable, since number of possible microscopic states should astronomically increases with increase of system size. Thus, a variety of calculation techniques have been developed to effectively address $\mathcal{C}$. One of the most successful techniques is Monte Carlo (MC) simulation with Metropolis algorithm, which samples important microscopic states contributing to $\mathcal{C}$, and the MC simulation have been subsequently modified such as multihistogram method, multicanonical ensembles and entropic sampling in order to effectively sweep across the configuration space. One of the exceptions is coherent potential approximation, where it considers the average occupation of elements with the lack of information about geometrical structure. Another is high-temperature expansion enabling efficient estimation of energy as well as other physical properties at high temperature.

When we consider classical systems, typically their constituents are spatially constrained in various ways. For instance, crystal lattice acts as constraint for substitutional crystalline solids, and volume and density as constraints for liquids in rigid box. Although the existing theoretical approaches amply predict macroscopic physical property and structure in equilibrium metallic and semiconductor alloys based on first-principles calculations, the role of the spatial constraint on equilibrium properties do not get sufficient attention so far. Following this fact, our recent studies find new representation of macroscopic physical properties (including internal energy, density, and free energy) and of macroscopic structure for disordered states, by using a few number of specially selected microscopic states. We find that these special microscopic states depend only on the type of spatial constraint, and are independent of constituent elements, multibody interactions, and of temperature, which means that we can a priori know the structure of the special microscopic states. We have demonstrated that this finding provides significantly efficient and systematic prediction of equilibrium properties for multicomponent alloys based on first-principles calculation. This important characteristics for equilibrium properties rely on the fact that statistical independence for density of microscopic states (DOMS) in configuration space appears numerically vanished at thermodynamic limit for a wide class of spatial constraints, whereas such behavior of the DOMS have not been quantitatively well-understood so far. In the present article, we theoretically tackle this problem based on the Random Matrix with Gaussian Orthogonal Ensemble, where corresponding statistical independence is mathematically guaranteed.

II. METHOD AND DISCUSSIONS

Let us first briefly explain the density of microscopic states (DOMS) on configuration space for non-interacting system. As shown in Fig. I we find in the present study that for a wide class of spatial constraints, DOMS for large number of constituents with multicomponent system can be universally well-characterized by a multidimensional gaussian distribution, namely,

$$g(q_1, \ldots, q_k) \simeq \frac{1}{2\pi^2 |\Gamma|^{1/2}} \exp \left[ -\frac{1}{2} \cdot H \Gamma^{-1} H^\dagger \right],$$

where $\{q_1, \ldots, q_k\}$ denotes complete basis functions to describe possible microscopic states, $H$ is the $g$-component vector of $(q_1 - \langle q_1 \rangle_1, \ldots, q_k - \langle q_k \rangle_1)$ where $\langle \cdot \rangle_1$ denotes tak-
ing arithmetic average over configuration space, and \( \Gamma \) represents covariance matrix for \( g(q_1, \ldots, q_N) \), reflecting the spatial constraint. This means that under a proper set of basis functions to give diagonal \( \Gamma \), statistical interdependence practically vanishes, although in principle, basis functions themselves are not statistically independent due to the existence of spatial constraint.\(^\text{16}\)

\[
|\phi\rangle = \sum_p |p\rangle \langle p| \phi\rangle .
\] (3)

In binary system where occupation of elements is specified by Ising-like spin of \( \sigma \pm 1 \), coefficient of the basis function \(|p\rangle\) can be simply given by

\[
\langle p| \phi\rangle = \prod_{k \in \alpha_p} \sigma_k^\phi
\] (4)

where product \( k \) is taken for “figure” \( \alpha_p \) along \(|p\rangle\), consisting of corresponding lattice points, and \( \langle \cdot \rangle_\phi \) denotes linear average over symmetry-equivalent figure to \( \alpha_p \) on microscopic state \(|\phi\rangle\). The advantage to employ the generalized Ising model is that for binary system, we confirm that the basis functions above can provide diagonal \( \Gamma \) for any combination of corresponding figures at equiatomic composition: We do not need to further find a set of basis functions to diagonalize \( \Gamma \). Here, we therefore prepare equiatomic binary system on fcc lattice, where basis functions along up to 6th nearest-neighbor (6NN) pairs and all triplets consisting of up to 6NN pairs are considered, resulting in 29 basis functions. In a similar fashion to the random matrix, we construct DOMS constructed from the 29 basis functions by performing Monte Carlo (MC) simulation to uniformly sampling microscopic states (500,000 MC step) for 256, 2048, and 3024-atom MC cell to see the system-size dependence of the DOMS. Variance of DOMS projected onto individual coordination is all normalized to one so that diagonal elements of resultant covariance matrix all take one.

\[
\langle p| \phi\rangle = \prod_{k \in \alpha_p} \sigma_k^\phi
\] (4)

In binary system where occupation of elements is specified by Ising-like spin of \( \sigma \pm 1 \), coefficient of the basis function \(|p\rangle\) can be simply given by

\[
\langle p| \phi\rangle = \prod_{k \in \alpha_p} \sigma_k^\phi
\] (4)

where product \( k \) is taken for “figure” \( \alpha_p \) along \(|p\rangle\), consisting of corresponding lattice points, and \( \langle \cdot \rangle_\phi \) denotes linear average over symmetry-equivalent figure to \( \alpha_p \) on microscopic state \(|\phi\rangle\). The advantage to employ the generalized Ising model is that for binary system, we confirm that the basis functions above can provide diagonal \( \Gamma \) for any combination of corresponding figures at equiatomic composition: We do not need to further find a set of basis functions to diagonalize \( \Gamma \). Here, we therefore prepare equiatomic binary system on fcc lattice, where basis functions along up to 6th nearest-neighbor (6NN) pairs and all triplets consisting of up to 6NN pairs are considered, resulting in 29 basis functions. In a similar fashion to the random matrix, we construct DOMS constructed from the 29 basis functions by performing Monte Carlo (MC) simulation to uniformly sampling microscopic states (500,000 MC step) for 256, 2048, and 3024-atom MC cell to see the system-size dependence of the DOMS. Variance of DOMS projected onto individual coordination is all normalized to one so that diagonal elements of resultant covariance matrix all take one.

\[
\langle p| \phi\rangle = \prod_{k \in \alpha_p} \sigma_k^\phi
\] (4)

where product \( k \) is taken for “figure” \( \alpha_p \) along \(|p\rangle\), consisting of corresponding lattice points, and \( \langle \cdot \rangle_\phi \) denotes linear average over symmetry-equivalent figure to \( \alpha_p \) on microscopic state \(|\phi\rangle\). The advantage to employ the generalized Ising model is that for binary system, we confirm that the basis functions above can provide diagonal \( \Gamma \) for any combination of corresponding figures at equiatomic composition: We do not need to further find a set of basis functions to diagonalize \( \Gamma \). Here, we therefore prepare equiatomic binary system on fcc lattice, where basis functions along up to 6th nearest-neighbor (6NN) pairs and all triplets consisting of up to 6NN pairs are considered, resulting in 29 basis functions. In a similar fashion to the random matrix, we construct DOMS constructed from the 29 basis functions by performing Monte Carlo (MC) simulation to uniformly sampling microscopic states (500,000 MC step) for 256, 2048, and 3024-atom MC cell to see the system-size dependence of the DOMS. Variance of DOMS projected onto individual coordination is all normalized to one so that diagonal elements of resultant covariance matrix all take one.

\[
\langle p| \phi\rangle = \prod_{k \in \alpha_p} \sigma_k^\phi
\] (4)

where product \( k \) is taken for “figure” \( \alpha_p \) along \(|p\rangle\), consisting of corresponding lattice points, and \( \langle \cdot \rangle_\phi \) denotes linear average over symmetry-equivalent figure to \( \alpha_p \) on microscopic state \(|\phi\rangle\). The advantage to employ the generalized Ising model is that for binary system, we confirm that the basis functions above can provide diagonal \( \Gamma \) for any combination of corresponding figures at equiatomic composition: We do not need to further find a set of basis functions to diagonalize \( \Gamma \). Here, we therefore prepare equiatomic binary system on fcc lattice, where basis functions along up to 6th nearest-neighbor (6NN) pairs and all triplets consisting of up to 6NN pairs are considered, resulting in 29 basis functions. In a similar fashion to the random matrix, we construct DOMS constructed from the 29 basis functions by performing Monte Carlo (MC) simulation to uniformly sampling microscopic states (500,000 MC step) for 256, 2048, and 3024-atom MC cell to see the system-size dependence of the DOMS. Variance of DOMS projected onto individual coordination is all normalized to one so that diagonal elements of resultant covariance matrix all take one.
random matrix and practical system. For random matrix, we first numerically construct \( l \times m \) random matrix where constituent elements are obtained by normal numbers as described above. Here, to make comparison with the practical system, we respectively give \( l = 29 \) and \( m = 500,000 \). To check the validity, we compare the DOEs of the constructed Random Matrix and those obtained through the characteristics of Marcenko-Pastur distribution, where corresponding DOE of covariance matrix can be analytically determined with \( l \to \infty \) and \( m \to \infty \), where the ratio of \( l/m \) is kept fixed. We confirm that the DOEs for the constructed Random Matrix discussed below exhibits excellent agreement with the analytical ones.

Figure 2 compares the resultant DOEs for random matrix and for practical systems with different number of constituents, \( N \). We can see that when the system size is small (i.e., \( N = 32 \)), landscape of the DOE appears completely different from that for Random Matrix. Especially, density of states around \( \varepsilon = 0 \) comes from the significant statistical interdependence between chosen basis functions due to the periodic boundary condition. Meanwhile, when \( N \) increases, landscape of DOEs for practical systems appears gradually close to that for random matrix having single sharp peak with non-zero finite width around \( \varepsilon = 1 \). Particularly, several sub-peaks below \( \varepsilon = 1 \) for practical systems are significantly diminished when \( N \) increases. The highest peaks of DOEs around \( \varepsilon = 1 \) for random matrix as well as for practical systems can be naturally attributed to the fact that trace of covariance matrix for random matrix and for practical systems take exactly the same value. To further make quantitative comparison, we estimate lower-order (from 2nd to 4th) moment of the DOEs. Figure 3 shows system-size dependence of the resultant 2nd, 3rd and 4th moment of DOEs for practical system, together with that for random matrix represented by dashed horizontal lines. We can clearly see that when \( N \) increases, value of all moments for practical system approaches to that for random matrix. These results therefore indicate that when the number of microscopic states around the center of gravity of DOMS in configuration space increase with increase of the system size, statistical interdependence along each coordination can be vanished: This certainly supports our developed approach using a few special microscopic states, which uses this characteristics of statistical interdependence to decompose contribution from each coordinate to macroscopic physical properties.

To summarize, by using the characteristics of random matrix consisting of independently random numbers, we confirm that statistical interdependence of density of microscopic states in configuration space tend to disappear when the system size increases. This result support our developed approach to provide new representation for equilibrium macroscopic properties, based on the disappearance of the statistical interdependence for large systems.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Materials Science on Synchrozed LPSO Structure” (26109710) and a Grant-in-Aid for Young Scientists B (25820323) from the MEXT of Japan, Research Grant from Hitachi Metals Materials Science Foundation, and Advanced Low Carbon Technology Research and Development Program of the Japan Science and Technology Agency (JST).

---

1. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).
2. A.M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. 63, 1195 (1989).
3. G. Bhanot, R. Salvador, S. Black, P. Carter, and R. Toral, Phys. Rev. Lett. 59, 803 (1987).
4. J. Lee, Phys. Rev. Lett. 71, 211 (1993).
5. M. Jaros, Rep. Prog. Phys. 48, 1091 (1985).
6. F.Y. Wu, Rev. Mod. Phys. 54, 235 (1982).
7. N.A. Zarkevich and D.D. Johnson, Phys. Rev. Lett. 92, 255702 (2004).
8. A. Franceschetti, S.V. Dudiy, S.V. Barabash, A. Zunger, J. Xu and M. van Schilfgaarde, Phys. Rev. Lett. 97, 047202 (2006).
9. T. Mueller and G. Ceder, Phys. Rev. B 82, 184107 (2010).
10. J. P. Julien, P.E.A. Turchi and D. Mayou, Phys. Rev. B 64, 195119 (2001).
11. A. van de Walle, Nature Mater. 7, 455 (2008).
12. G.L.W. Hart, V. Blum, M.J. Walorski and A. Zunger, Nature Mater. 4, 391 (2005).
13. C.C. Fischer, K.J. Tibbetts, D. Morgan and G. Ceder, Nature Mater. 5, 641 (2006).
14. K. Yuge, J. Phys. Soc. Jpn. 84, 084801 (2015).
15 K. Takeuchi, R. Tanaka and K. Yuge, J. Phys.: Condens. Matter 27, 385201 (2015).
16 D. de Fountain, *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic Press, Cambridge, Massachusetts, 1994), Vol. 47, pp. 33?176.
17 J.M. Sanchez, F. Ducastelle, and D. Gratias, Physica **128A**, 334 (1984).