

Distribution of Equilibrium Free Energies in a Thermodynamic System with Broken Ergodicity*

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Abstract At low temperatures the configurational phase space of a macroscopic complex system (e.g., a spin-glass) of $N \sim 10^{23}$ interacting particles may split into an exponential number $\Omega_s \sim \exp(\text{const} \times N)$ of ergodic sub-spaces (thermodynamic states). It is usually assumed that the equilibrium collective behavior of such a system is determined by its ground thermodynamic states of the minimal free-energy density, and that the equilibrium free energies follow the distribution of exponential decay. But actually for some complex systems, the equilibrium free-energy values may follow a Gaussian distribution within an intermediate temperature range, and consequently their equilibrium properties are contributed by excited thermodynamic states. Based on this analysis, the re-weighting parameter y in the cavity approach of spin-glasses is easily understood. Depending on the free-energy distribution, the optimal y can either be equal to or be strictly less than the inverse temperature β .

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1 Introduction

A thermodynamic system contains a huge number N of interacting particles, with N typically in the order of 10^{23} or larger. The microscopic configurations of such a system changes with time in a complicated and stochastic manner under the joint action of internal forces and perturbations from the environment. At the macroscopic level the collective properties of the system are, on the other hand, essentially time-invariant and can be described by only a few phenomenological parameters such as the mean energy density and the specific heat. Nevertheless, at certain values of the temperature T or other environmental control parameters, the macroscopic behavior of the system may also change abruptly and qualitatively. Such phase-transition phenomena, being a major research branch of statistical mechanics for many years, are deeply connected with the break down of the ergodicity property of the system.^[1,2]

For a large class of complex systems with quenched disorder (heterogeneity) and frustrations in the interactions among particles as best represented by spin-glasses,^[3] when ergodicity breaks down, exponentially many thermodynamic states will form, each of which corresponds to one ergodic sub-space of the whole configurational space of the system.^[4] For these systems, it is widely believed (see, e.g., Refs. [4] ~ [7]) that, the *equilibrium* properties of the system are determined by the *ground* thermodynamic states, which have the global minimal free-energy density f_{\min} , and the distribution of equilibrium free-energies follows an exponential law. The *excited* thermodynamic states of free-energy densities $f > f_{\min}$ are regarded as irrelevant as long as equilibrium properties are concerned,

although they dominate the out-of-equilibrium dynamics of the system (see, e.g., Refs. [8] ~ [11]). For example, a disordered p -spin interaction Ising model ($p \geq 3$)^[12,13] is known to have an ergodic–non-ergodic transition at a temperature T_d (the so-called dynamic transition temperature), but it is expected that the equilibrium spin-glass phase transition will occur only at a lower temperature T_s (the static transition temperature). For $T_d > T > T_s$, although there are exponentially many thermodynamic states, all the relevant configurations for the equilibrium properties are still assumed to reside in the same ergodic sub-space of the whole configuration space.

In this paper, we argue that these statements may not necessarily be correct. Through a general theoretical analysis, we show that the equilibrium free-energy densities of an ergodicity-broken system may actually follow a Gaussian distribution with a mean value larger than f_{\min} . Then the equilibrium behavior of the system will be determined by a group of excited thermodynamic states rather than by the ground thermodynamic states. Our statement is further supported by analytical and simulation results on an exactly solvable model system. This work helps to clarify that, the excited thermodynamic states of a system of broken ergodicity are important not only to the dynamical (non-equilibrium) properties of the system but also to its equilibrium properties. Although the physical picture of ergodicity-breaking and proliferation of metastable states has been well known in the communities of spin-glasses, structural glasses, and super-cooled liquids for many years (see, for example, Refs. [4] and [14]), by explicitly pointing out the possibility of a Gaussian-formed equilibrium

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free-energy distribution, this paper helps us to understand more deeply the equilibrium (static) properties of spin-glasses and other complex systems. Especially, the physical meaning of the re-weighting parameter y in the cavity-approach of mean-field spin-glasses at the level of first-step replica-symmetry-breaking^[15,16] can be easily understood in terms of the equilibrium free-energy distribution. The optimal value of y is either equal to the inverse temperature β (for Gaussian free-energy distributions) or strictly less than β (for exponential free-energy distributions).

When the equilibrium free-energies of an ergodicity-broken system follows a Gaussian distribution, the ground thermodynamic states of the system may not be reached by any dynamical process, no matter how long one waits or which specific cooling schedule is used. In other words, equilibrium studies based on the Gibbs measure will give a dynamics-independent lower-bound on the reachably free-energy density. We hope this work will shed light on further studies of various fascinating dynamic behaviors of complex systems.^[8–11,17]

2 General Theoretical Analysis

The configuration of a general classical system of N particles can be denoted by $\vec{\sigma} \equiv \{\sigma_1, \sigma_2, \dots, \sigma_N\}$, where the configurational variable σ_i of a particle does not need to be discrete or be scalar. Each configuration has an energy $\mathcal{H}(\vec{\sigma})$. Starting from an initial configuration, the system evolves with time and forms a stochastic trajectory in the whole configurational space Γ of the system. At sufficiently high temperatures the system is ergodic and its trajectory will visit all the (relevant) configurations in Γ if waiting long enough. More precisely we say a system is ergodic if two trajectories evolved from a pair of randomly chosen initial configurations will, with probability unity, intersect with each other. In this ergodic situation the total partition function of the system is expressed as

$$Z(\beta) = \sum_{\vec{\sigma} \in \Gamma} \exp(-\beta \mathcal{H}(\vec{\sigma})), \quad (1)$$

where $\beta \equiv 1/T$ is the inverse temperature. When the system reaches equilibrium, its free energy is minimized, but its total internal energy still fluctuates with time. If many measurements are performed on the internal energy, one will realize that the measured energy values follow a Gaussian distribution,^[1,2]

$$\rho(E) = \sqrt{\frac{\beta^2}{2\pi C_E(\beta)}} \exp\left(-\frac{\beta^2}{2C_E(\beta)}(E - \langle E \rangle)^2\right), \quad (2)$$

where $\langle E \rangle$ and $C_E(\beta)$ are, respectively, the mean total energy and the specific heat of the system. Both $\langle E \rangle$ and $C_E(\beta)$ are proportional to N .

At low temperatures, however, ergodicity may no longer hold. As the environmental perturbations become weak, the system may be impossible to overcome the large

free energy barriers between different regions of the configurational space Γ ; it is then trapped in one of many ergodic sub-spaces Γ_α of Γ . In this ergodicity-broken case, a sub-space Γ_α is referred to as a thermodynamic state of the system, which has an equilibrium free energy F_α as given by

$$F_\alpha(\beta) = -\beta^{-1} \log\left(\sum_{\vec{\sigma} \in \Gamma_\alpha} e^{-\beta \mathcal{H}(\vec{\sigma})}\right). \quad (3)$$

The energy distribution Eq. (2) still holds in each thermodynamic state α , but now both $\langle E \rangle$ and $C_E(\beta)$ are thermodynamic state α -dependent.

When there are more than one thermodynamic state, the total partition function (1) can be re-expressed as a summation over all the thermodynamic states,

$$Z(\beta) = \sum_{\alpha} \exp(-\beta F_\alpha(\beta)), \quad (4)$$

with each thermodynamic state α contributing a term $\exp(-\beta F_\alpha)$. Equation (4) contains all the information about the equilibrium properties of an ergodicity-broken system. It has the same form as Eq. (1), but with the configurations $\vec{\sigma}$ being replaced by the thermodynamic states α . This equation indicates that the contribution of a thermodynamic state α to the equilibrium property of the system is proportional to $\exp(-\beta F_\alpha(\beta))$. Although such a Gibbs measure is arguably not holding in an out-of-equilibrium dynamics, it is commonly used in equilibrium studies. In this work we also stick to this Gibbs measure.

To further understand this Gibbs measure, in this paragraph we try to give an interpretation based on a gedanken dynamical process of heating and annealing (but we emphasize that the results of this paper is independent of this interpretation). For the system to escape a thermodynamic state α , a large external perturbation has to be applied. This might be achieved by first heating the system and then cooling it.^[18,19] As the system is heated to a high temperature, it becomes ergodic and memory about its prior history is lost. After the system is cooled down slowly to its original low temperature, it may reach a different thermodynamic state α' at the end of this process. (During the annealing process of this gedanken experiment, the system may be driven by a global and parallel dynamical rule.) All the thermodynamic states of the system at a low temperature T will therefore be explored if one repeats extremely many times this heating-annealing experiment. With this external assistance, the system again becomes ergodic at the level of thermodynamic states. Since the prior history of the system is completely destroyed in the heating-annealing experiment, the frequency of the system reaching a thermodynamic state α is supposed to be given by the Gibbs measure $e^{-\beta F_\alpha}/Z(\beta)$.

Let us denote by $\Omega_s(F)$ the total number of thermodynamic states in the system with free energy F . Then the equilibrium free energy distribution is governed by

$$P(F) \propto \Omega_s(F) e^{-\beta F} = \exp(-\beta F + S_s(F)), \quad (5)$$

where, $S_s(F) = \log \Omega_s(F)$ is the entropy at the level of thermodynamic states. $S_s(F)$ is a concave and increasing function of F . We are interested in systems with exponentially many thermodynamic states, i.e., systems with $S_s(F)$ being proportional to the size N in leading order.

If at the minimal free energy $F_{\min}(\beta)$, the first derivative of $S_s(F)$ is greater than β , i.e., $S'_s(F_{\min}) > \beta$, there exists a free energy value $F = \bar{F} > F_{\min}(\beta)$ such that $S'_s(\bar{F}) = \beta$. At the vicinity of \bar{F} , the entropy $S_s(F)$ is expressed as

$$S_s(F) = S_s(\bar{F}) + \beta(F - \bar{F}) - \frac{\beta^2}{2C_F(\beta)}(F - \bar{F})^2. \quad (6)$$

After inserting Eq. (6) into Eq. (5) we find that, at equilibrium, the probability of being in a state of free energy F is governed by the following Gaussian distribution,

$$P(F) = \sqrt{\frac{\beta^2}{2\pi C_F(\beta)}} \exp\left(-\frac{\beta^2}{2C_F(\beta)}(F - \bar{F})^2\right). \quad (7)$$

From Eq. (7) it is clear that \bar{F} is the mean free energy value of the equilibrium thermodynamic states, and $C_F(\beta) \propto N$ characterizes the fluctuation of the equilibrium free energies. Since $\bar{F}(\beta) > F_{\min}(\beta)$, we conclude that the equilibrium properties of the system at inverse temperature β are determined by those excited thermodynamic states whose free energy density $f(\beta) = \bar{F}/N$ is larger than the minimal free energy density $f_{\min}(\beta) = F_{\min}/N$. The ground thermodynamic states of free energy density $f_{\min}(\beta)$ actually do not contribute to the equilibrium properties of the system.

On the other hand, if the entropy $S_s(F)$ has the property that at $F = F_{\min}(\beta)$ its first derivative is less than β , i.e.,

$$S'(F_{\min}) = x\beta \quad (8)$$

with $0 \leq x < 1$, then equation (5) suggests that the equilibrium free energies will follow an exponential law:

$$P(F) \propto e^{-\beta(1-x)(F-F_{\min}(\beta))}, \quad F \geq F_{\min}(\beta). \quad (9)$$

Consequently, the equilibrium properties of the system will be contributed by the ground thermodynamic states of free energy density $f_{\min}(\beta)$; and the fluctuation of the observed free energies is only of order unity.

3 Grand Free Energy

To treat the two free-energy distributions of the preceding section with the same mathematical framework, we need to define a grand free energy for the system. Following the work of Mézard, Parisi, and Zecchina^[15,16] on the mean-field theory of $T = 0$ spin-glasses, we can decouple

microscopic configurations and macroscopic states by introducing an artificial inverse temperature y at the level of thermodynamic states. The system's grand free energy $G(\beta; y)$ ^[19] is defined by

$$G(\beta; y) \equiv -y^{-1} \log\left(\sum_{\alpha} e^{-yF_{\alpha}(\beta)}\right) \quad (10)$$

$$= -y^{-1} \log\left[\int df e^{N(\Sigma(f)-yf)}\right]. \quad (11)$$

In the thermodynamic limit of $N \rightarrow \infty$, the grand free energy density is

$$g(\beta; y) \equiv \lim_{N \rightarrow \infty} \frac{G(\beta; y)}{N}. \quad (12)$$

In Eq. (11), $\Sigma(f) \equiv S_s(Nf)/N$ measures the entropy density at the level of thermodynamic states; it is called the complexity of the system at free energy density f .^[16] The adjustable parameter y controls which thermodynamic states will contribute to the grand free energy $G(\beta; y)$. Equation (11) indicates that, when the re-weighting parameter y is not too large, the grand free energy is contributed by the excited thermodynamic states of free energy density satisfying $\Sigma'(f) = y$. The relevant free energy density and complexity are related to the grand free energy density by

$$f(\beta; y) = \frac{\partial yg(\beta; y)}{\partial y}, \quad (13)$$

$$\Sigma(\beta; y) = y^2 \frac{\partial g(\beta; y)}{\partial y} > 0. \quad (14)$$

On the other hand, when $y > y^*(\beta) \equiv \Sigma'(f_{\min}(\beta))$, the grand free energy is contributed by the ground thermodynamic states of the system, therefore

$$f(\beta; y > y^*(\beta)) = f_{\min}(\beta), \quad (15)$$

$$\Sigma(\beta; y > y^*(\beta)) = 0. \quad (16)$$

From Eqs. (14) and (16) we know that, (i) the minimal free energy density $f_{\min}(\beta)$ corresponds to $y = y^*(\beta)$, where the complexity $\Sigma(\beta; y)$ drops to zero; (ii) if $\Sigma(\beta; \beta) > 0$, then $f(\beta; \beta) > f_{\min}(\beta)$ is the mean free energy density of the thermodynamic states which dominate the equilibrium properties of the system.

4 Results on p -Spin Interaction Ising Spin-Glass Model

Let us complement the above-described general analysis with a concrete example, namely the p -spin interaction Ising model on a complete graph.^[13] The Hamiltonian of the model is

$$\mathcal{H}(\sigma) = - \sum_{1 \leq i_1 < \dots < i_p \leq N} J_{i_1 i_2 \dots i_p} \sigma_{i_1} \sigma_{i_2} \dots \sigma_{i_p}, \quad (17)$$

where the spin variables $\sigma_i = \pm 1$ and the quenched (time-independent) coupling constant $J_{i_1 \dots i_p}$ is identically and

independently distributed according to

$$\omega(J_{i_1 i_2 \dots i_p}) = \sqrt{\frac{N^{p-1}}{\pi p! J^2}} \exp\left(-\frac{N^{p-1}}{p! J^2} J_{i_1 i_2 \dots i_p}^2\right) \quad (18)$$

with J being a constant parameter (the energy unity of the system). For $p = 2$, equation (17) is the celebrated Sherrington–Kirkpatrick model.^[4,20] For $p \geq 3$, earlier efforts^[5,13] have found that the system has two transitions, a dynamic transition followed by a lower-temperature static transition. The dynamic transition is related to the onset of ergodicity-breaking and is important for out-of-equilibrium processes, but it was not regarded as a

real equilibrium phase-transition. An extended version of the model (17) was investigated by Kirkpatrick and Thirumalai^[14] twenties years ago concerning possible connections between dynamical and equilibrial properties.

If we assume that all the thermodynamic states of the model system (17) are evenly distributed in the whole configurational space Γ , i.e., there is no further clustering of the thermodynamic states, the grand free-energy density of the system as defined by Eq. (12) can be obtained through the cavity method^[4] (see also Ref. [19]). The final expression for $g(\beta; y)$ is

$$g(\beta; y) = -\frac{1}{\beta} \log 2 - \frac{p-1}{4} J^2 (y q_0^p + (\beta - y) q_1^p) - \frac{1}{4} \beta J^2 (1 - p q_1^{p-1}) - \frac{1}{y} \int \frac{dz_0}{\sqrt{\pi}} e^{-z_0^2} \log \left[\int \frac{dz_1}{\sqrt{\pi}} e^{-z_1^2} \cosh^{y/\beta} (\beta J \lambda_0 z_0 + \beta J \lambda_1 z_1) \right], \quad (19)$$

where $\lambda_0 = \sqrt{p} q_0^{(p-1)/2}$, $\lambda_1 = \sqrt{p} (q_1^{p-1} - q_0^{p-1})^{1/2}$, $q_0 = \langle m \rangle^2$, and $q_1 = \langle m^2 \rangle$, with m being the magnetization of a vertex in one thermodynamic state, and $\langle \dots \rangle$ means averaging over all the thermodynamics states α of the system (each of them is weighted with the factor $e^{-y F_\alpha(\beta)}$). q_0 and q_1 satisfy $\partial g / \partial q_0 = \partial g / \partial q_1 = 0$. Equation (19) was first derived in Ref. [12] using the replica trick, and was regarded as the free-energy density of the system.^[12,13] But we see that actually $g(\beta; y)$ is the grand free-energy density, which combines both the free energy effect and the entropy effect (at the level of thermodynamic states) of the system.

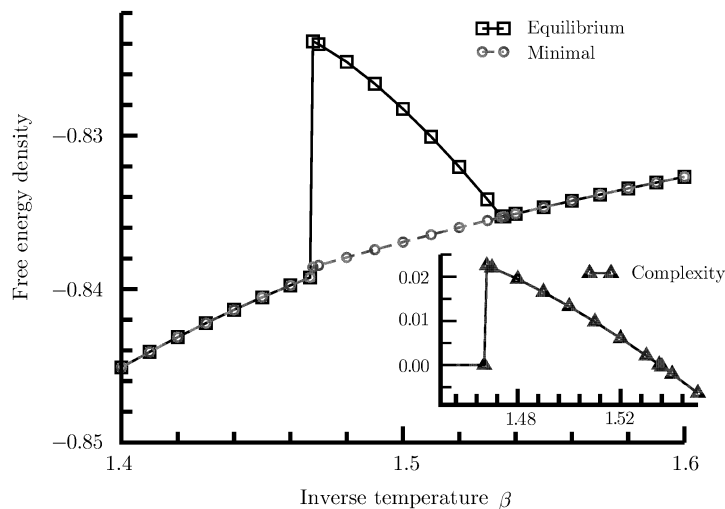


Fig. 1 The mean equilibrium free energy density and the minimal free energy density of the 3-spin interaction Ising model (17) on a complete graph of $N = \infty$. Inset shows the complexity $\Sigma(\beta; \beta)$ as a function of β . For $\beta \in (1.468, 1.5352)$ the equilibrium properties of the system are determined by excited thermodynamic states.

For an infinite system with $p = 3$, the mean values of the equilibrium and the minimal free energy density are shown in Fig. 1 as a function of the inverse temperature β . Ergodicity of the system breaks down at $\beta_1 \simeq 1.468$, where the whole configuration space splits into exponentially many ergodic sub-spaces. The equilibrium and the minimal free energy density of the system has a jump at β_1 , but the energy and grand free-energy densities are both continuous at this point. For $\beta_1 < \beta < \beta_2 \simeq 1.5352$,

the mean equilibrium free-energy density is higher than the minimal free-energy density (which is obtained by setting $y > \beta$), and the complexity of the system decreases continuously with β and drops to zero at β_2 . For $\beta > \beta_2$, the mean equilibrium free-energy density is identical to the minimal free energy density of the system. The above-mentioned results also hold when one considers the possibility of further clustering of the thermodynamic states or splitting of each thermodynamic state into

sub-states.^[13,21]

For a system with small size N ergodicity will be preserved even at low temperatures; but the relevant configurations of the system may show some degree of clustering. To detect this organization, we can calculate the overlaps between the sampled independent configurations of the system. The overlap of two configurations $\vec{\sigma}^1$ and $\vec{\sigma}^2$ is defined as^[4]

$$\Lambda_{12} = \frac{1}{N} \sum_{j=1}^N \sigma_j^1 \sigma_j^2. \quad (20)$$

The overlap histograms for two finite systems of sizes $N = 100$ and $N = 200$ are shown in Fig. 2. Two peaks appear in the histograms when β approaches the theoretically predicted value β_1 . The peak at $\Lambda \simeq 0$ is due to pairs of configurations from different domains of the configurational space, and the other peak at $\Lambda \simeq 0.8$ (for $N = 100$) or $\Lambda \simeq 0.6 \sim 0.8$ (for $N = 200$) corresponds to the overlaps between configurations from the same domain of the configurational space. Figure 2 also demonstrates that, as the system size N increases, the organization of the configurational phase space becomes more complex.

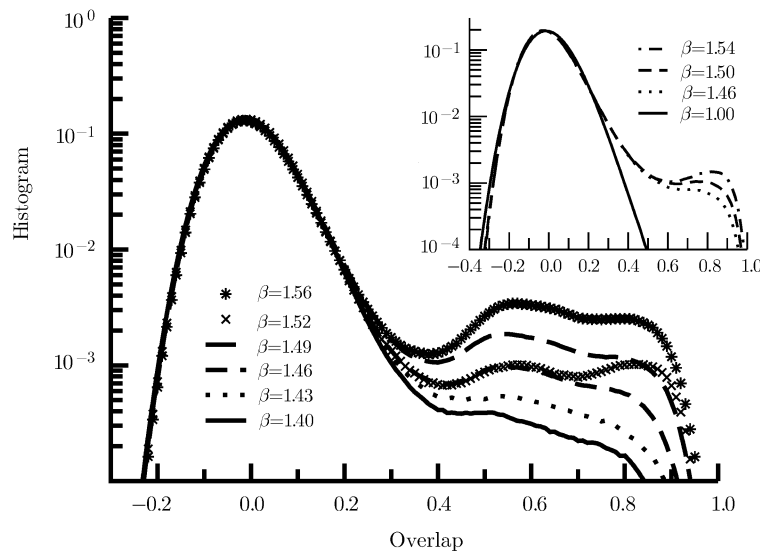


Fig. 2 Overlap histograms for a 3-spin interaction Ising systems of $N = 200$ vertices (the main figure) and $N = 100$ vertices (the inset). Different curves correspond to different inverse temperatures.

5 Conclusion and Discussion

In this paper we studied the equilibrium properties of a thermodynamic system with broken ergodicity such as a spin-glass. If the number of thermodynamic states increases exponentially fast with the system size N at low temperatures, we show that the equilibrium free-energy distribution of the system may be Gaussian, and consequently the equilibrium static properties of the system are determined by excited thermodynamic states of the system, whose free-energy densities are higher than the minimal free-energy density of the system. A grand free energy function (with an adjustable parameter y) was defined in this paper following the earlier work of Refs. [15] and [16] to calculate the mean value of the equilibrium free-energy density and the complexity of the system. In terms of the equilibrium free-energy distribution, the physical meaning of the parameter y is also easily understood. The optimal value of y is either equal to the inverse temperature β (for Gaussian free-energy distribution) or strictly less than β (for exponential free-energy distribution).

The mean-field theory of spin-glasses by Parisi and colleagues^[4,7] was based on the assumption that the equilibrium free-energies of the system obey an exponential distribution. Under that theory, only the thermodynamic states of the ground free-energy density are *allowed* to contribute to the equilibrium properties of the system. As we now know, for disordered systems with two-body interactions^[20] this assumption of exponential-distribution is valid. But for a system with many-body interactions, there may exist a temperature window within which the free-energy distribution is Gaussian. In this later case, figure 1 demonstrates that the mean value of the equilibrium free-energy densities *decreases* with temperature. This apparently will cause an entropy crisis, but actually the entropy of a thermodynamic state is positive. Notice that when the free-energy distribution is Gaussian, different groups of thermodynamic states are taking the dominant role as the temperature changes. The predictions of the present work can be further checked by Monte

Carlo simulations on a large finite-connectivity complex system with many-body interactions.

In this work, we focused on the equilibrium statistical properties of an ergodicity-broken system and assumed that the significance of each thermodynamic state α is proportional to $\exp(-\beta F_\alpha)$, with F_α being its free energy. This assumption may not be valid for out-of-equilibrium dynamical processes. For these later non-equilibrium processes, it has been suggested that the system will typically be trapped to a free energy level which corresponds to the maximal complexity. When the system is cooled down slowly from a high temperature, the reachable thermodynamic states depend strongly on the specific dynamical rules used.^[10,11] The mean equilibrium free energy density

discussed in this paper, although may not being achievable in a dynamical experiment, sets a lower-bound on the dynamically reachable free energy density. As demonstrated by Fig. 1, in an intermediate temperature range, this lower bound may be well above the minimal free energy density of the system.

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