I. INTRODUCTION

Statistical mechanics describes the average properties of a system without referring to all its microscopic states. In most situations, the validity of the canonical statistical description is guaranteed in the thermodynamic limit, which requires that, while the degrees of freedom of the heat bath is infinite, the system-bath coupling approaches infinitesimal. However, if the system only interacts with a small heat bath with finite degrees of freedom, the system-bath interaction cannot be ignored compared with the energy of the heat bath. The properties of such a finite system have recently attracted a lot of attention with regard to both experiments [1,2] and theories [3–11]. Initiated from the pioneering work of Gibbs, the canonical statistics until now has been built on a rigorous foundation. However, with reference to the conventional canonical way, the obtained noncanonical distribution reflects the back action of system on the bath and thus depicts the statistical correlations between two subsystems by the mutual information as a result of energy conservation.

II. FINITE SYSTEM-BATH COUPLING

We generally consider a composite coupled system, which can be divided into a system $S$ with Hamiltonian $H_S$ and a heat bath $B$ with Hamiltonian $H_B$. The coupling between the system and the bath can be generally described by $H_I$. Then we have the total Hamiltonian $H = H_S + H_B + H_I$. The system and the bath have the following spectrum decompositions:

$$H_S = \sum_n E_n |n\rangle\langle n|,$$

$$H_B = \sum_{j=1}^N \epsilon_{kj} |kj\rangle\langle kj| \otimes \prod_{i \neq j} I_i. \tag{2}$$

Here $|n\rangle$ is the eigenstate of the system with the corresponding eigenenergy $E_n$. The heat bath is composed of $N$ noninteracting particles, the eigenstate of the $j$th particle is $|kj\rangle$ with the corresponding eigenenergy $\epsilon_{kj}$, and $I_i$ is the identity operator of the Hilbert space of the $i$th particle. In the following, we will use the notation $|\tilde{k}\rangle = \prod_{j=1}^N |j\rangle$, $\tilde{k} = (k_1,k_2,\ldots,k_N)$, to present the eigenstate of $H_B$ and denote $\epsilon(\tilde{k}) = \sum_{j=1}^N \epsilon_{kj}$ as its eigenenergy. Usually, the energy spectrum of the system is much sparser than the heat bath, i.e.,

$$\min |E_n - E_m| \gg \max |\epsilon(\tilde{k}) - \epsilon(\tilde{l})|, \tag{3}$$

which holds for the neighboring energy levels $n$ and $m$ ($\tilde{k}$ and $\tilde{l}$) of the system (bath) (see Fig. 1).

The system-bath interaction $H_I$ is weak compared to $H_0$, which reads

$$H_I = \sum_{j=1}^N \sum_{n,n',k,j',k'} g_{nk,j,n'k',j'} |n,k\rangle\langle n',k'| \otimes \prod_{i \neq j} I_i \tag{4}$$

in the perturbation theory; via this Hamiltonian the noncanonical statistical distribution without referring to any specific model is presented. To further illustrate the novel thermodynamic properties of the finite system by noncanonical statistics, a model of coupled harmonic oscillators is introduced in Sec. III, and the statistical quantities such as internal energy, fluctuation, and the mutual information between two subsystems are calculated. We conclude in Sec. IV.
with \(|n, k_j\rangle \equiv |n\rangle \otimes |k_j\rangle\). To obtain the canonical density matrix \(\rho_S\) of the system, we usually start with a microcanonical density matrix of the system and its heat bath, \(\rho_{\text{mic}}\), without considering \(H_I\), and then trace over the heat bath, i.e., \(\rho_S = \text{Tr}_B \rho_{\text{mic}}\). The density matrix \(\rho_{\text{mic}}\) describes a microcanonical ensemble which is assumed in an energy shell \([E, E + \delta]\) with \(\delta\) a small energy scale, \(\delta \ll E\), and

\[
V(E, \delta) = \text{Span}\{|n, \vec{\delta}\rangle : E \leq E_n + \epsilon(\vec{\delta}) \leq E + \delta\}
\]

is the subspace of \(H_S + H_B\) associated with this energy shell, and \(P_{V(E, \delta)}\) is the projection operator to \(V(E, \delta)\). Then the probability of finding the state \(|n\rangle\) in this canonical ensemble is

\[
P_n(E) = \langle n| \rho_S |n\rangle = \frac{\Omega(E, E_n, \delta)}{\text{dim} \ V(E, \delta)},
\]

where \(\Omega(E, E_n, \delta) = \text{dim} \ V_n(E, E_n, \delta)\) and

\[
V_n(E, E_n, \delta) = \text{Span}\{|n, \vec{\epsilon}\rangle : E - E_n \leq \epsilon(\vec{\epsilon}) \leq E - E_n + \delta\}
\]

represents the subspace of \(H_S + H_B\) associated with the subenergy shell \([E - E_n, E - E_n + \delta]\) when the system state is fixed at \(|n\rangle\), obviously, \(V(E, \delta) = \sum_n \bigoplus V_n(E - E_n, \delta)\).

In certain cases that the heat bath is no longer infinitely large, and the system-bath interaction energy is small but should not be complete neglected, the reduced density matrix of the system can be obtained by perturbatively considering \(H_I\). The first-order perturbation effect of these off-diagonal terms with \(n \neq n'\) can be ignored under the condition

\[
|g_{nk_j, n'k'_j}(\epsilon_{k'_j} - \epsilon_{k_j})| \ll 1.
\]

However, for the terms with \(n = n'\), the above condition \(|g_{nk_j, n'k'_j}(\epsilon_{k'_j} - \epsilon_{k_j})| \ll 1\) will be violated due to the properties of the energy spectra given in Eq. (3). Thus the diagonal terms can contribute to the system behaviors and should be kept in the interaction Hamiltonian [16], which yields

\[
H_I \approx \sum_{j=1}^{N} \sum_{n, k_j} g_{nk_j, n'k'_j} |nk_j\rangle \langle n'k'_j| \otimes \prod_{i \neq j} I_i.
\]
of $\Omega(E,\delta)$ is dependent on the Hamiltonian $H$; thus with or without the considering of $H_1$, the deformation of energy shell yields $\Omega(E,\delta)$ and $\tilde{\Omega}(E,\delta)$ have different expressions. Therefore, we should keep in mind that $S(E)$ is actually a functional of $V(E,\delta)$, i.e., $S(E) \equiv \mathbb{S}[V(E,\delta)]$. When the system is in the state $|n\rangle$, the entropy can be expanded as [18]

$$
\hat{S}(E - E_n) = S(E - E_n) + \delta_n S(E - E_n) \\
\approx S(E) - \frac{\partial S(E)}{\partial E} E_n + \phi_n, \quad (16)
$$

where

$$
\phi_n = \delta_n S(E) - \frac{\partial [\delta_n S(E)]}{\partial E} E_n. \quad (17)
$$

The term $\delta_n S(E - E_n)$ is the functional variation of $S(E - E_n)$, where the subscript $n$ means that the functional variation also depends on the state of system. In the above derivation, we actually assume a small deformation of the energy shell, i.e., when $N$ is large, there is a small difference between $\Omega(E,\delta)$ and $\tilde{\Omega}(E,\delta)$. This difference vanishes in the thermodynamic limit as shown in Ref. [4] for a concrete example. As $E_n$ is still small compared with $E$, then we can expand $S(E - E_n)$ to the first order, and $\phi_n$ represents the first-order approximation of $\delta_n S(E - E_n)$. The derivative terms of $S(E)$ can be evaluated by the idea from classical phase space: Since $\Omega(E)$ is the dimension of the subspace $V(E,\delta)$, it is proportional to the volume of the energy shell in the phase space. In a $N$-dimensional space, the volume confined in an isoenergetic surface of energy $E$ can be considered as the volume of a $N$-dimensional polyhedron with effective radius $E$, which is proportional to $E^N$, where $\xi$ is a dimensionless real number independent of $N$ and is usually related to the degeneracy of the system. Therefore, the volume of the energy shell is given by

$$
\Omega(E) \propto (E + \delta)^N - E^N, \quad (18)
$$

which leads to

$$
\beta(E) = \frac{\partial S(E)}{\partial E} = \frac{k_B(\xi N - 1)}{E}. \quad (19)
$$

With the thermodynamic relations, $\beta = (k_B T)^{-1}$ and $T$ is the temperature of the system in equilibrium. Obviously, Eq. (19) recovers the equipartition theorem $E \approx \xi N k_B T$, i.e., each degree of freedom contributes $\xi k_B T$ to the total energy. Therefore, the noncanonical distribution reads

$$
\hat{P}_n(E) = \frac{1}{Z} e^{-\beta E_n + \phi_n/k_B}, \quad (20)
$$

where $Z = \sum \exp(-\beta E_n + \phi_n/k_B)$ is the partition function.

If the interaction energy could be neglected compared with the total energy $E$, the variation terms $\phi_n$ containing $\delta_n S(E)$ in Eq. (20) can be dropped and thus naturally lead to the usual canonical form,

$$
P_n(E) = \frac{1}{Z} e^{-\beta E_n}. \quad (21)
$$

Otherwise, the deformation of energy shell which leads to $\phi_n$ will shift the system energy level and thus modify $P_n(E)$. Usually $\phi_n$ cannot be calculated easily; however, for some special models (one of which will be introduced in the next section), we can find a simple expression for $\phi_n$.

### III. ILLUSTRATION WITH HARMONIC OSCILLATORS SYSTEM

Now we consider a coupled harmonic oscillators system as an example to illustrate the statistical thermodynamic properties of a finite system. The system $S$ is a single harmonic oscillator with eigenfrequency $\omega$ and $a^\dagger(a)$ as its creation (annihilation) operator. The heat bath is generally modeled as a collection of harmonic oscillators with Hamiltonian $H_B = \sum_{j=1}^N \omega_j b_j^\dagger b_j$. Here $b_j^\dagger(b_j)$ is the creation (annihilation) operator of the oscillator with frequency $\omega_j$. In the weak-coupling limit, we can assume the effective system-bath interaction as

$$
H_I = \sum_{j=1}^N \lambda_j a^\dagger a (b_j^\dagger + b_j). \quad (22)
$$

This Hamiltonian is usually used to describe the interaction between a single mode light field and mechanical oscillators in optical-mechanical system [19–21].

In this model, the eigenvalues of the total Hamiltonian are

$$
E(n, m(n)) = n \omega + \Delta_n + \sum_{j \neq n} m_j \omega_j, \quad (23)
$$

which corresponding to the eigenstates $|n, m(n)\rangle = |n\rangle \otimes \prod_{j \neq n} |m_j(n)\rangle$. The eigenstate of the heat bath $|m_j(n)\rangle$ is defined as a displaced Fock state $|m_j(n)\rangle = D(-\lambda_j n/\omega_j)|m_j\rangle$, with the displacement operator $D(a_j) = \exp(\alpha a_j^\dagger - \alpha^* a_j)$. Here the deformation of the energy shell is described by an $n$-dependent factor,

$$
\Delta_n = -\sum_{j=1}^N \frac{\lambda_j^2 n^2}{\omega_j} \equiv -\kappa n^2. \quad (24)
$$

Therefore, in this model the deformation of each subenergy shell is only related to $\Delta_n$, which is independent of the specific state of the heat bath. Then the deformed energy shell is simply related with the original energy shell without considering $H_I$ by

$$
\tilde{V}_n(E - E_n, \delta) = V_n(E - \Delta_n - E_n, \delta). \quad (25)
$$

Further, the function form of $\tilde{S}(E - E_n)$ is the same as $S(E - E_n)$ by only substituting $E$ with $E - \Delta_n$:

$$
\tilde{S}(E - E_n) = S(E - \Delta_n - E_n). \quad (26)
$$

Then the functional variation $\delta_n S(E)$ can be calculated by the usual differential to the first order,

$$
\delta_n S(E) \approx \frac{\partial S(E)}{\partial E} \Delta_n. \quad (27)
$$

Together with the results in Eq. (20), the noncanonical distribution is given by

$$
\tilde{P}_n(E) = \frac{1}{Z} e^{-\beta (n\omega - \kappa n^2 - \xi n^2)}, \quad (28)
$$

where

$$
\xi = \frac{\partial^2 S(E)}{\partial E^2} = -\frac{k_B(\xi N - 1)}{E^2}. \quad (29)
$$

The square and cubic terms of $n$ in the exponent of $\tilde{P}_n(E)$ greatly change the statistical distribution from the canonical
distribution \( P_n(E) = Z^{-1} \exp(-\beta n \omega) \), especially for large \( n \). However, Eq. (28) does not apply to very large \( N \) for the following reason: The total energy \( E \) of the system and the heat bath is conserved, and the heat bath energy should always be non-negative \( \sum_{m,j} m_j \omega_j > 0 \). Thus, the energy shell of \( V_n(E - \Delta_n - E_n, \delta) \) constrains the system energy level by \( E \geq E_n \), which implies \( n < (\omega - \sqrt{\omega^2 - 4\kappa E})/(2\kappa) \).

Therefore, for such coupled system, the maximum energy level for the system is
\[
\kappa n_{\text{max}} = \left\lfloor \frac{\omega - \sqrt{\omega^2 - 4\kappa E}}{2\kappa} \right\rfloor,
\]
where \( \lfloor x \rfloor \) represents the maximum integer below \( x \).

Usually \( \kappa \) is much smaller than \( \omega \), thus the noncanonical statistics distribution \( \tilde{P}_n(E) \) for low energy levels does not differ much from the canonical one, as shown in Fig. 3. However, as \( |\Delta_n| \) grows with \( n^2 \), the high energy levels have more populations than those in the canonical distribution, which can be seen from the inset of Fig. 3. We choose the system eigenfrequency as unit \( \omega = 1 \), the total energy \( E = 100 \), and \( \kappa = 0.00235 \). According to Eq. (30), the highest energy level is \( n_{\text{max}} = 160 \) in this situation. The canonical distribution is plotted by set \( \kappa = 0 \) in \( \tilde{P}_n(E) \). A numerical research also gave the similar noncanonical distribution for coupled spin systems [22].

Because the high-energy states have relatively larger populations, the internal energy of the system
\[
U = \sum_{n=0}^{n_{\text{max}}} n \omega \tilde{P}_n(E)
\]
under the noncanonical statistics is larger than that under the canonical one. This fact is illustrated in Fig. 4, where the internal energy \( U \) is plotted with respect to \( \beta \). The distinction between the noncanonical and canonical statistics for \( U \) evidently appears when the inverse temperature \( \beta \) decreases and the interaction energy strength \( \kappa \) grows. As \( \beta \) approaches zero, the high-temperature limit of the internal energy \( U \) arrives at \( n_{\text{max}} \omega / 2 \), which is finite as the total energy is up-bounded by \( E \) for small heat bath. This differs substantially from the case in the thermodynamic limit: The average energy of a harmonic oscillator which contacts with an infinite heat bath will diverge when \( \beta \) decreases to zero.

Another feature reflecting the nonmonotony of the noncanonical distribution is the relative fluctuation of the system internal energy
\[
\langle \Delta U \rangle^2 = \frac{1}{U^2} \sum_{n=0}^{n_{\text{max}}} (n \omega - U)^2 \tilde{P}_n(E).
\]

![Figure 3](image1.png)

**FIG. 3.** (Color online) The noncanonical (blue solid line) and canonical (pink dashed line) distribution functions for coupled oscillators system. We choose \( \omega = 1, E = 100, \beta = 0.5, \) and \( \kappa = 0.00235 \). The highest energy level is \( n_{\text{max}} = 160 \). The noncanonical and canonical distributions are similar for low energy levels while they differ greatly for high energy levels.

![Figure 4](image2.png)

**FIG. 4.** (Color online) The internal energy \( U \) of the system with respect to \( \beta \) for noncanonical and canonical statistics. We plot the cases of \( \kappa = 0.002, n_{\text{max}} = 138 \) (blue solid line); \( \kappa = 0.0015, n_{\text{max}} = 122 \) (orange dotted-dash line); \( \kappa = 0.001, n_{\text{max}} = 112 \) (pink dashed line); and the canonical case for \( \kappa = 0, n_{\text{max}} = 112 \). For small \( \beta \), the internal energy \( U \) is explicitly larger than that given by canonical statistics.

![Figure 5](image3.png)

**FIG. 5.** (Color online) The internal energy relative fluctuation \( \langle \Delta U \rangle^2 \) of the system with respect to \( \beta \) for noncanonical and canonical statistics. The parameters are chosen the same as Fig. 4. A local maximum appears in the energy fluctuation for small \( \beta \) which results of the noncanonical statistics.
As shown in Fig. 5, at both the low- and high-temperature limits, the noncanonical and canonical statistics of the system present similar fluctuation behavior. To characterize these two limits, we consider the system as a harmonic oscillator with truncated energy levels (the highest energy level is labeled by \(n_{\text{max}}\)) under canonical statistics (\(\kappa = 0\)), whose energy fluctuation is denoted as \((\Delta U_C)^2\). It is analytically calculated that in the low-temperature limits, the fluctuation \((\Delta U_C)^2 \approx \exp(\beta \Theta_0)\) is exactly the same as the result when \(n_{\text{max}} \to \infty\). Because the populations of the high-energy levels decrease significantly in the low temperature, only the several low-energy levels determine the thermodynamic behavior. In the high-temperature limit, the energy fluctuation behaves as

\[
(\Delta U_C)^2 \approx \frac{1}{3} + \frac{2}{3n_{\text{max}}} + \frac{n_{\text{max}}}{9}\beta, \tag{33}
\]

which is a linear function of \(\beta\). We remark here that the high-temperature limit and thermodynamic limit cannot commute with each other, as

\[
\lim_{n_{\text{max}} \to \infty} \lim_{\beta \to 0} (\Delta U_C)^2 = \frac{1}{3}, \tag{34}
\]

while

\[
\lim_{\beta \to 0} \lim_{n_{\text{max}} \to \infty} (\Delta U_C)^2 = 1. \tag{35}
\]

However, in the intermediate range of \(\beta\), a local maximum in energy fluctuation distinguishes the noncanonical distribution from the canonical one, especially for strong system-bath interaction \(\kappa\). This maximum can be qualitatively understood as follows: we can rewrite the noncanonical distribution as \(P_n(E) = Z^{-1} \exp(-\beta n \eta_n \omega)\), where \(\eta_n = 1 - \kappa \eta / \omega - \kappa \eta^2 / E\) is a positive factor for \(n \leq n_{\text{max}}\). As \(\eta_n \leq 1\), the reverse temperature \(\beta\) can be considered as effectively reduced by \(\eta_n\), thus the linear region for small \(\beta\) is enlarged in the noncanonical statistics. Based on the above observations, we know that the noncanonical statistics exhibits obviously novel effects when the interaction energy strength \(\kappa\) is large and the temperature is high.

Besides the high distribution tail for a single system, the noncanonical statistics provides other new characters when the system is composed of two independent subsystems \(l_1\) and \(l_2\). Even if these two subsystems do not directly interact with each other, the deformation of the energy shell can effectively result in a correlation between them. Here we still use harmonic oscillator (HO) systems for illustration. The system consists of two single-mode HOs with the Hamiltonian \(H_S = \sum_{k=1,2} \omega_k a_k^{\dagger} a_k\). The system interacts with a common small heat bath, which can be modeled by the Hamiltonian \(H_B = \sum_{j=1}^N \omega_j b_j^{\dagger} b_j\). The interaction term reads

\[
H_I = \sum_{k=1,2} \sum_{j=1}^N \lambda_{kj} a_k^{\dagger} a_k b_j^{\dagger} + b_j. \tag{36}
\]

Following the same discussion about the energy shell deformation for a single system, we can straightforwardly obtain the joint distribution of the composite system as

\[
\tilde{P}(E, E_{n_1}^{(1)}, E_{m_2}^{(2)}) = \frac{1}{Z_I} e^{-\beta(E_{\text{en}} + \Delta_{\text{en}}) + \xi \Delta_{\text{en}} E_{\text{en}}}, \tag{37}
\]

where \(E_{\text{en}} = n \omega_1 + m \omega_2\) and

\[
\Delta_{\text{en}} = \sum_{j=1}^N \frac{(\lambda_{1j} n + \lambda_{2j} m)^2}{\omega_j},
\]

\[
Z_I = \sum_{n,m} e^{-\beta(E_n + \Delta_{\text{en}}) + \xi \Delta_{\text{en}} E_{\text{en}}}. \tag{38}
\]

Here \(\sum_{n,m}\) means the summation of the system energy levels should satisfy the constrain \(0 \leq E_n + \Delta_{\text{en}} \leq E\). It can be seen from Eq. (37) that the statistics of two subsystems are not independent with each other due to the cross-term in \(\Delta_{\text{en}}\). This statistical correlation can be described by mutual information defined as

\[
S(l_1 : l_2) = S(l_1) + S(l_2) - S(l_1 + l_2), \tag{39}
\]

where the entropy

\[
S(l_k) = -\sum_{n=0}^{n_{\text{max}}} \tilde{P}(E, E_{n_1}^{(k)}, E_{m_2}^{(k)}) \ln \tilde{P}(E, E_{n_1}^{(k)}). \tag{40}
\]

Following the same discussion about the energy shell deformation for a single system, we can straightforwardly obtain the joint distribution of the composite system as

\[
\tilde{P}(E, E_{n_1}^{(1)}, E_{m_2}^{(2)}) = \frac{1}{Z_I} e^{-\beta(E_{\text{en}} + \Delta_{\text{en}}) + \xi \Delta_{\text{en}} E_{\text{en}}}, \tag{37}
\]

For simplicity, we assume the two HOs are identical with \(\omega_1 = \omega_2 \equiv \omega, \lambda_{1j} = \lambda_{2j} \equiv \lambda_j, \) and \(\kappa\) is defined the same as Eq. (24). As shown in Fig. 6, there appears to be a nonzero mutual entropy if we use noncanonical statistics to describe the composite system in a common small heat bath. In contrast, if the interaction energy is too small to be considered compared to the total energy, we can use the canonical distribution to calculate the mutual entropy, which naturally gives \(S(l_1 : l_2) = 0\), i.e., the two subsystems are not correlated with each other.
IV. CONCLUSION

We study the statistical thermodynamics of an open system whose interaction with the heat bath cannot be neglected. The interaction modifies the system energy shell and leads to the noncanonical density matrix for such a system. It is shown in a model that noncanonical distribution has a big “tail” for higher energy levels, which is the most significant difference from the canonical distribution. This noncanonical feature results in higher internal energy and energy fluctuation of the system. Moreover, different parts of the composite system are naturally correlated with each other, which is described by mutual entropy. We note that the noncanonical form of distribution may be related to the explanation of the black hole information paradox [23].

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