Introduction – Systems are inevitably interacting with the environments in which they are embedded. A system is referred to be small, if it is significantly affected by the surrounding environments. For small systems, classical thermodynamics, remarked by Einstein as “the only physical theory which I am convinced will never be overthrown within the framework of applicability of its basic concepts” [1], is not directly suitable since the non-extensiveness. In 1962, Hill proposed the nanothermodynamics [2, 3], which adds an subdivision potential term to the traditional Gibbs equation, reading

\[ E = U + \varepsilon \equiv TS - pV + \mu N + \varepsilon. \]  

(1)

Equation (1) is known as the Gibbs–Hill equation, where \( \varepsilon \) is nothing but the subdivision potential. This approach intrigues widespread interests among various fields of modern sciences [4–8].

For a system at finite temperature \( T \), with constant volume \( V \) and particle number \( N \), the Helmholtz free energy \( F = E - TS \) is related to partition function \( Z \) as

\[ F = -\beta^{-1} \ln Z. \]  

(2)

Throughout this paper, we set \( \beta = 1/(k_B T) \), with \( k_B \) and \( T \) being the Boltzmann constant and temperature, respectively. For simplicity, we always set \( k_B = 1 \) below.

For large systems, which is extensive due to the thermodynamic limit, \( Z \) characterizes the canonical ensemble, i.e.,

\[ Z = \text{tr}_S(e^{-\beta H_S}) \rightarrow \text{cf. Eq. (7)} \]  

(3)

with \( H_S \) being the system Hamiltonian. This will lead to \( \varepsilon = 0 \), resulting \( E = U \) in Eq. (1). However, small systems are not distributed canonically due to their interactions with the environments, and in these cases Eq. (3) is violated and \( \varepsilon \neq 0 \). It is therefore necessary to modify the \( Z \) in Eq. (3) and distinguish between \( E \) and \( U \).

Subdivision potential proportional to the difference between the thermal and von Neumann entropies – Now turn to the discussion on the subdivision potential \( \varepsilon \) of small systems. Since the system is small, as explained above, the environment and the system–environment interaction are necessarily involved. Consider a system–plus–environment composite Hamiltonian reading

\[ H_T = H_S + H_{SB} + h_B, \]  

(4)

where \( H_S, H_{SB} \) and \( h_B \) are the system, the system–environment interaction and the environment Hamiltonians, respectively. To identify the subdivision potential \( \varepsilon \), one may follow Landsberg and introduce the temperature–dependent Hamiltonian \( H_S(\beta) \) as [9, 10]

\[ H_S(\beta) \equiv -\beta^{-1}\left[ \ln \text{tr}_B(e^{-\beta H_T}) - \ln Z_B \right]. \]  

(5)

with \( Z_B = \text{tr}_B(e^{-\beta h_B}) \). In this formalism, the system density operator is

\[ \rho_S(\beta) = \frac{e^{-\beta H_S(\beta)}}{Z} = \frac{\text{tr}_B(e^{-\beta H_T})}{Z_T}. \]  

(6)

where the partition functions are [cf. Eq. (3)]

\[ Z = \text{tr}_S(e^{-\beta H_S(\beta)}) = \frac{Z_T}{Z_B} \]  

and \( Z_T = \text{Tr}(e^{-\beta H_T}) \). (7)

In this paper, \( \text{Tr} \), \( \text{tr}_S \) and \( \text{tr}_B \) represent the total trace, the system and the environmental subspace partial trace, respectively. Since the bath is less affected by the system, we identify the \( E \) as difference between the energy of total system \( E_T \) and that of bath \( E_B \), leading to the equality

\[ E = E_T - E_B = -\frac{\partial \ln(Z_T/Z_B)}{\beta} = -\frac{\partial \ln Z}{\beta}. \]  

(8)

where \( E_T = -\partial \ln Z_T/\beta \) and \( E_B = -\partial \ln Z_B/\beta \). On the other hand, the thermodynamic internal energy of system \( U \) is considered as the average of \( H_S(\beta) \), namely

\[ U = \langle H_S(\beta) \rangle = Z^{-1}\text{tr}_B[H_S(\beta)e^{-\beta H_S(\beta)}]. \]  

(9)

Therefore, we can identify the subdivision potential as [cf. Eqs. (1), (8) and (9)]

\[ \varepsilon = -\frac{\partial \ln Z}{\beta} - \langle H_S(\beta) \rangle = \beta \left\langle \frac{\partial H_S(\beta)}{\partial \beta} \right\rangle. \]  

(10)

To exhibit the temperature dependence of \( \varepsilon \), we first rewrite \( \langle H_S(\beta) \rangle \) as

\[ \langle H_S(\beta) \rangle = -\beta^{-1}\left\{ \text{tr}_S[\rho_S(\beta) \ln \rho_S(\beta)] + \ln Z \right\}, \]  

(11)

and it together with Eq. (10) shows that

\[ \varepsilon = \beta^{-1}[S_{\text{therm}}(\beta) - S_N(\beta)] \]  

(12)
with the thermal entropy:

\[ S_{\text{therm}}(\beta) = -\frac{\partial F}{\partial T} = \beta^2 \frac{\partial F}{\partial \beta}, \]  

and the von Neumann entropy:

\[ S_{\text{vNe}}(\beta) = -\text{tr}[\rho_\beta(\beta) \ln \rho_\beta(\beta)]. \]  

Here, the free–energy \( F \) is defined in Eq. (2) with partition function \( Z \) in Eq. (7). Apparently, Eq. (12) tells us that the subdivision potential \( \varepsilon \) is proportional to the difference between the thermal entropy \( S_{\text{therm}}(\beta) \) and the von Neumann entropy \( S_{\text{vNe}}(\beta) \), as defined in Eqs. (13) and (14), respectively. It is reasonable to render the difference arises from that the thermodynamic limit is not satisfied for small systems.

**Thermodynamic integration** – Now, we apply the thermodynamic integration for the free energy \( F \), as done in our previous works [11, 12]. Consider a \( \lambda \)–augmented form of Eq. (4), reading

\[ H_\lambda(\lambda) = H_S + \lambda H_{SB} + h_b, \]  

with \( \lambda \in [0,1] \) characterizing the hybridization. Consider the a hybridization process with respect to \( \lambda \), at a constant temperature \( T \), as depicted in Fig. 1. The free energy change can be written in the integration form [11, 12]

\[ \Delta F(T) = F(T; \lambda = 1) - F(T; \lambda = 0), \]

\[ = \int_0^1 \frac{d\lambda}{\lambda} \text{Tr}[\rho(T; \lambda) \lambda H_{SB} \rho(T; \lambda)], \]  

with \( \rho(T; \lambda) = e^{-\beta H_T(\lambda)} / Z_T(\beta; \lambda) \).

We can obtain \( \Delta F(T) \) in Eq. (16) according to the Kirkwood thermodynamics integration as

\[ \Delta F(T) = \int_0^1 \frac{d\Delta F(T)}{d\lambda} d\lambda, \]

\[ = -\frac{1}{\beta} \int_0^1 \frac{d\lambda}{Z_T(\lambda)} \text{Tr}[\frac{d}{d\lambda} e^{-\beta(H_S + h_b + \lambda H_{SB})}]. \] (17)

It leads to \( \Delta F(T) \) in Eq. (16), due to the following relation:

\[ -\frac{1}{\beta} \text{Tr}\left[ \frac{d}{d\lambda} e^{-\beta(H_S + h_b + \lambda H_{SB})} \right] = \text{Tr}\left[ H_{SB} e^{-\beta(H_S + h_b + \lambda H_{SB})} \right]. \]

This relation is a special case of the general relation reading

\[ \text{Tr}\left[ \frac{d}{d\lambda} e^{O(\lambda)} \right] = \text{Tr}\left[ \frac{dO(\lambda)}{d\lambda} e^{O(\lambda)} \right], \]

which can be proved via the operator identity

\[ \frac{d}{d\lambda} e^{O(\lambda)} = \int_0^1 ds e^{(1-s)O(\lambda)} \frac{dO(\lambda)}{d\lambda} e^{O(\lambda)} \]

and the trace cyclic invariance.

As a result, Eqs. (10) and (16) give rise to

\[ \varepsilon(T) = T \left[ -\frac{\partial F(T; \lambda = 1)}{\partial T} - S_{\text{vNe}}(\beta) \right], \]

\[ = T \left[ -\frac{\partial \Delta F(T)}{\partial T} - \frac{\partial F(T; \lambda = 0)}{\partial T} - S_{\text{vNe}}(\beta) \right] \]

\[ = T[\Delta S_{\text{therm}}(T) - \Delta S_{\text{vNe}}(T)]. \] (18)

In Eq. (18), we have defined \( \Delta S_{\text{therm/vNe}}(T; \lambda = 1) - S_{\text{therm/vNe}}(T; \lambda = 0) \) and used the equality \( S_{\text{vNe}}(T; \lambda = 0) = S_{\text{therm}}(T; \lambda = 0) \) due to the canonicity in the absence of system–bath interactions. Numerically, all these quantities can be computed via the dissipation-equation-of-motion method (\( \Lambda \)-dynamics formalism or imaginary–time formalism) [11–13], which is a second quantization generalization of the well–known hierarchically equations of motion, serving as a rigid approach to the dynamics of a specific system coupled to the Gaussian environments [14–17].

**Example** – As an example, we consider a spin–boson model

\[ H_\lambda(\lambda) = (E \hat{\sigma}_z + V \hat{\sigma}_x) + \lambda \hat{\sigma}_z \hat{F} + h_b, \]  

with \( h_b \) being harmonic and the hybrid bath modes \( \hat{F} \) being linear, i.e., \( h_b = \frac{1}{2} \sum_j \omega_j (\hat{\sigma}_z^2 + \hat{\sigma}_x^2) \) and \( \hat{F} = \sum_j \omega_j \hat{\sigma}_x \).

The computational results are shown in Fig. 2, with parameters given in the caption. In Fig. 2, we show the temperature dependence of \( \varepsilon(T) \), as well as \( \Delta S_{\text{therm}}(T) \) and \( \Delta S_{\text{vNe}}(T) \). The temperature is scaled by the system charasteristic frequency \( \Omega_s \equiv 2 \sqrt{E^2 + V^2} \) [18]. It is observed that the subdivision potential exhibits a turnover near the characteristic frequency, and this is conjectured as a universal feature.

**Summary** – In summary, we first identify the subdivision potential \( \varepsilon \) to be proportional to the difference between the thermal and von Neumann entropies, followed by the establishment of its quantum thermodynamic integration. We explicitly show its temperature–dependence by taking the spin–boson model as an example, and one characteristic turnover point of subdivision potential is observed. Besides, the method developed in this work
FIG. 2: Temperature–dependence of the subvivision potential. Parameters are taken in accordance to that in Ref. [11]. The bath spectral density \( J(\omega) = (\pi/2) \sum_j c_j^2 \delta(\omega - \omega_j) \) takes the Drude form as \( J(\omega) = \eta \gamma \omega / (\omega^2 + \gamma^2) \) with parameters: \( \gamma = 4V \) and \( \eta = 0.5V \). The spin energy difference is \( E = 0.5V \), and the temperature is scaled by the system characteristic frequency \( \Omega_S \equiv 2\sqrt{E^2 + V^2} \).

serves as a versatile tool to help analyze the origin of non-extensiveness in nanosystems.

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