Main finding: The **equilibrium state** of a **quantum system, strongly coupled** with an **anharmonic environment**, shows **universal traits** independent of the details of the environment.

Ultrastrong coupling limit to quantum mean force Gibbs state for anharmonic environment

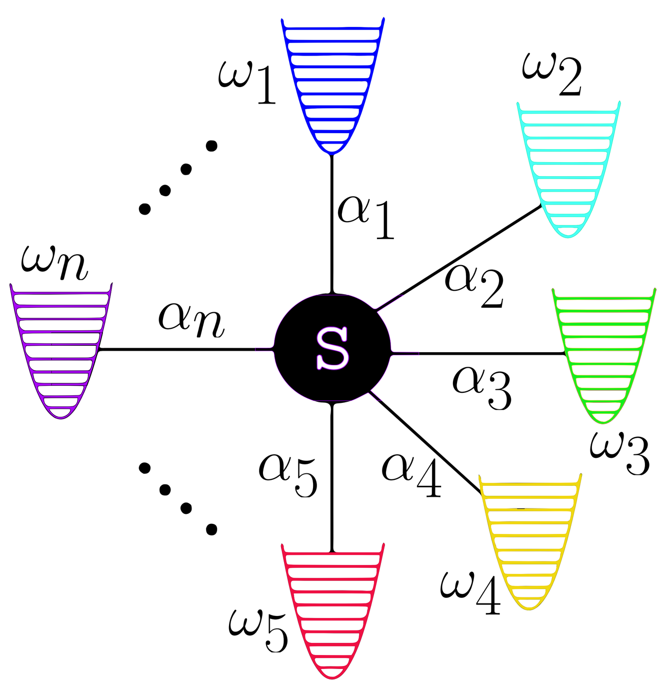
Motivation

1. **Generalized equilibrium state** of a quantum system deviates from the textbook Gibbs state at non-negligible **system-environment (SE) coupling** [1].
2. The analytical expression for this state for harmonic environment model with large SE coupling is known [2, 3].
3. However, the harmonic environment assumption is not always accurate [4]. The present work generalizes this result to more general SE models [5].

Results

1. The expression for the generalized equilibrium state remains unchanged even after significant **anharmonic generalization** of the environment.
2. For an even larger class of SE models, although the state deviates from the harmonic result, the basis in which it diagonalizes remains unchanged.

The harmonic environment model



This model involves a quantum system coupled to many uncoupled harmonic oscillators. The full SE Hamiltonian is given as $\hat{H}_{SE} = \hat{H}_S + \hat{H}_{\bar{S}}$, where $\hat{H}_S$ is the free system Hamiltonian and

$$\hat{H}_{\bar{S}} = \sum_k \left[\frac{\hat{p}_k^2}{2m_k} + \frac{1}{2}m_k\omega_k^2\left(\hat{q}_k - \alpha_k\hat{A}\right)^2\right]. \tag{1}$$

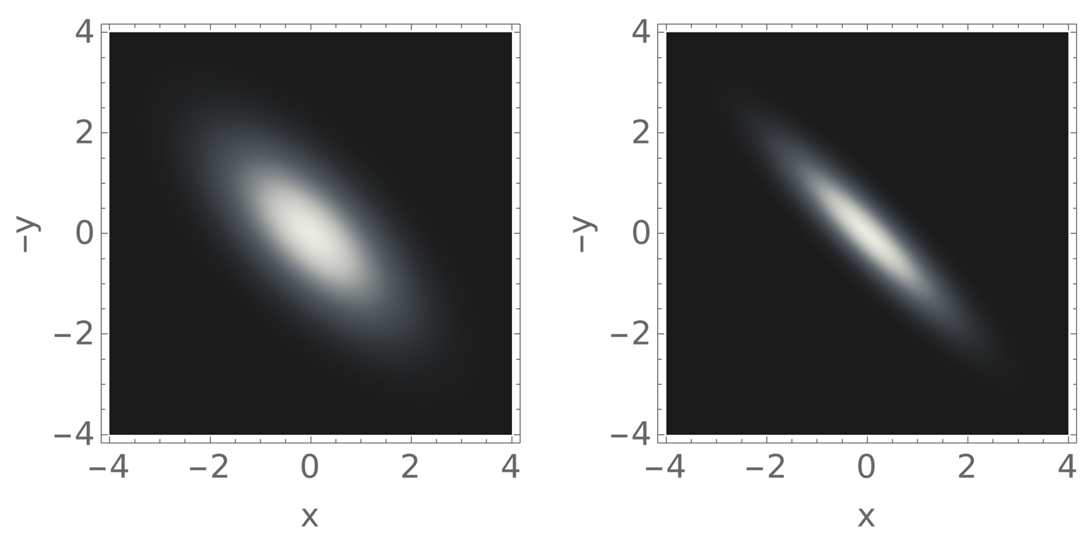
Here, $\hat{p}_k$ and $\hat{q}_k$ are the momentum and position operator of the kth environment particle, and $\hat{A}$ is a system operator.

Generalized equilibrium state

Generalized equilibrium state of a system, given the SE Hamiltonian $\hat{H}_{SE}$ at inverse temperature β, is formally defined as:

$$\hat{\rho}_{eq} = Z^{-1}\mathrm{Tr}_E\left[e^{-\beta\hat{H}_{SE}}\right]. \tag{2}$$

The following image plots the equilibrium state, $\rho(x, y)$, for a harmonic oscillator in position basis (which is known exactly for arbitrary SE coupling), as we increase the coupling strength (from left to the right image).



Strong coupling equilibrium state

The **strong coupling (SC) limit** is defined as $\lim \alpha_k \to \infty$ and the corresponding equilibrium state has been recently determined to be [3]

$$\hat{P}_i\hat{\rho}_{SC}\hat{P}_j = Z^{-1}\delta(i,j)\exp\left\{-\beta\hat{P}_i\hat{H}_S\hat{P}_i\right\}, \tag{3}$$

where $\hat{P}_i$ is the projection operator on the ith degenerate subspaces of $\hat{A}$ ($\hat{P}_i$ being 1D projectors in the case of no degeneracy).

Why anharmonic environment model?

The harmonic environment model is known to fail for many physical setups, for example, in the case of **electron transfer** happening in the presence of

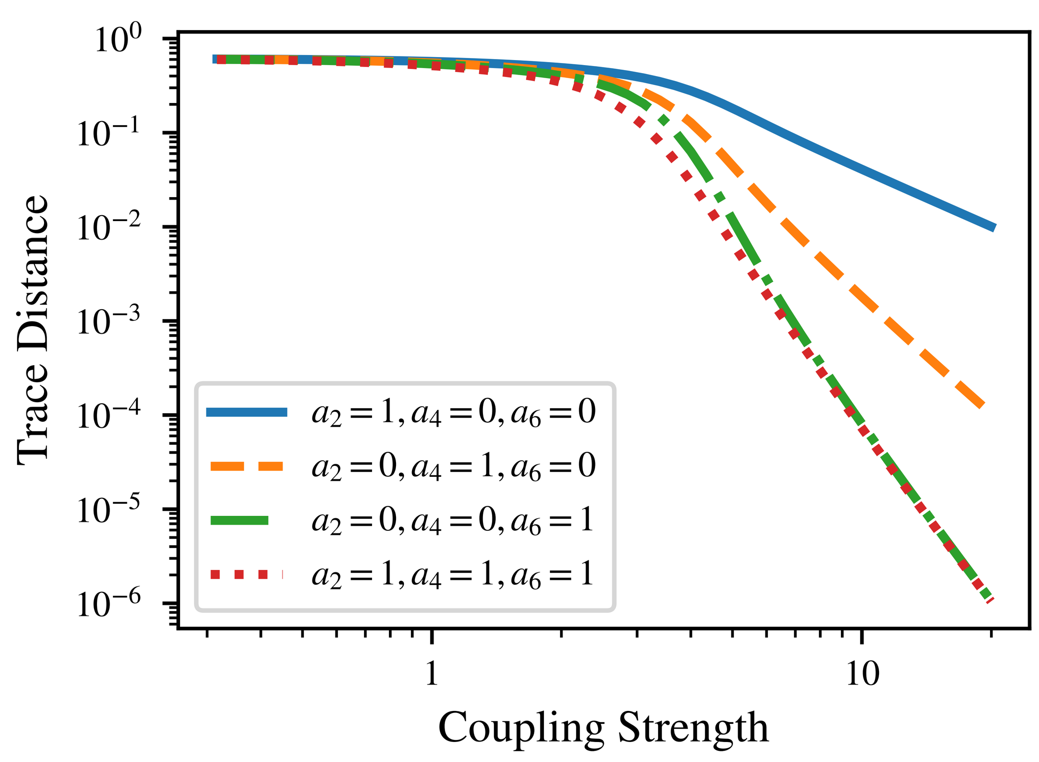
1. strongly coupled **low-frequency intramolecular modes**, or,
2. an environment consisting of **nonpolar liquids** (see, for example, [4]).

Generalization: GCL2 Model

If we generalize Eq. 1 as following [6]

$$\hat{H}_{\bar{S}} = \sum_k \left[\frac{\hat{p}_k^2}{2m_k} + U_k(\hat{q}_k - \alpha_k\hat{A})\right], \tag{4}$$

then, under some physical assumption on the interaction potential $U_k(x)$, we prove that the SC equilibrium state (Eq. 3) **remains unchanged**!



This figure plots, for a specific qutrit system, the trace distance between the SC equilibrium state proposed here and the numerically evaluated equilibrium state as a function of the coupling strength, for $U_k(x) = \sum_{n=1}^{3} a_{2n}x^{2n}$ in Eq. 4. We note that the trace distance vanishes in the large coupling limit, irrespective of the form of $U_k(x)$.

Intuitive Proof: In the path integral approach, Eq. 4 gives rise to the following action

$$S_k = \int_0^\beta dt\left\{\frac{m_k}{2}\dot{q}_k(t)^2 + U_k(q_k(t) - \alpha_k A(t))\right\}. \tag{5}$$

In the SC limit ($\alpha_k \to \infty$), small variations in $A(t)$ cause large changes in the argument of $U_k(x)$, giving rise to large potential energy cost to that path, unless we have $q_k(t) \approx \alpha_k A(t)$. But, in the latter case, the kinetic energy cost ($m_k\dot{q}_k(t)^2/2$) of that path blows up instead. Either way, in SC limit, $A(t) =$ constant is intuitively imposed, which leads to the SC equilibrium state (Eq. 3). See the paper for the detailed proof [5].

Further Generalizations: GCL Model

If we further generalize Eq. 1 as following,

$$\hat{H}_{\bar{S}} = \sum_k \left[\frac{\hat{p}_k^2}{2m_k} + V_k(\hat{q}_k, \alpha_k\hat{A})\right], \tag{6}$$

then, under some physically motivated assumptions on the form of $V_k(x, y)$, we find that although the form of the equilibrium state does change to

$$\hat{P}_i\hat{\rho}_{SC}\hat{P}_j = Z^{-1}\delta(i,j)\exp\left\{-\beta\hat{P}_i\hat{H}_S\hat{P}_i\right\}\mathrm{Tr}e^{-\beta\hat{H}_I(A_i)}, \tag{7}$$

it still **diagonalizes in the basis of $\hat{A}$**. Here, the only difference being the extra A_i dependent factor $\mathrm{Tr}e^{-\beta\hat{H}_I(A_i)}$, where A_i is the eigenvalue of $\hat{A}$ corresponding to $\hat{P}_i$.

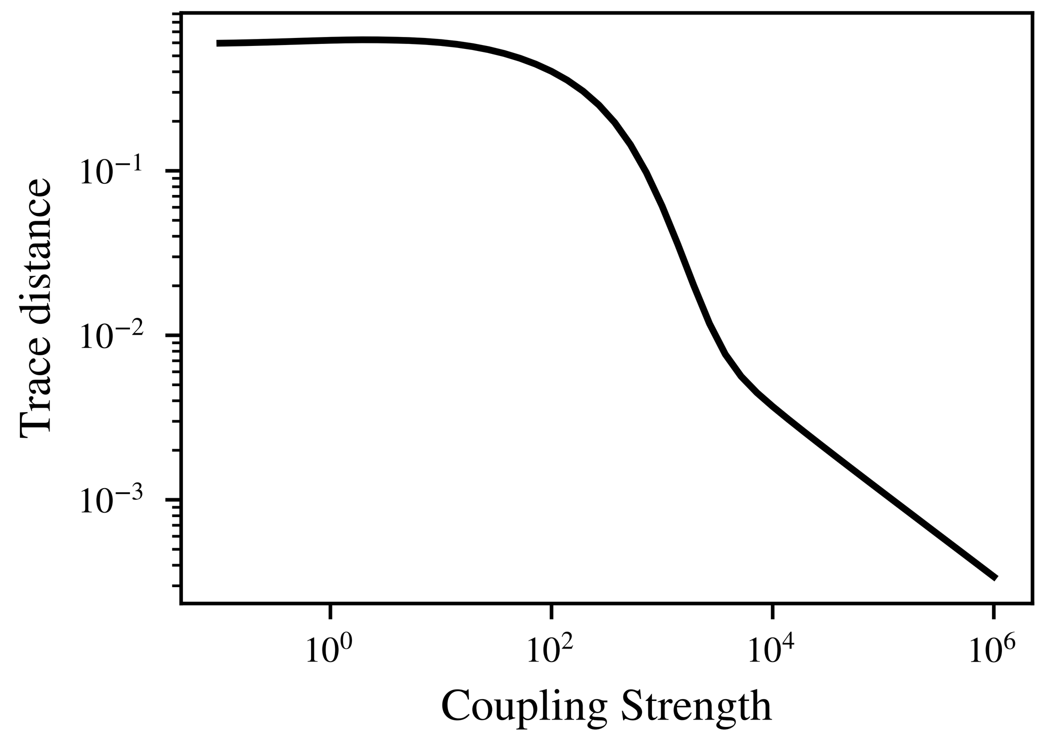
Zwanzig Model

For a different class of SE model with $\hat{H}_{\bar{S}}$ given as [7]

$$\hat{H}_{\bar{S}} = \sum_{k=1}^{N}\left[\frac{\hat{p}_k^2}{2m_k} + U_k^{\mathrm{free}}(\hat{q}_k) + \frac{\alpha_k}{2}U_k(\hat{q}_k - \hat{A})\right], \tag{8}$$

under the assumption that $U_k(x)$ has a unique global minima at $x = 0$, the equilibrium state is again found to **diagonalize in the basis of $\hat{A}$**.

For a discrete system, the equilibrium state has the same form as the harmonic environment case (Eq. 3), albeit for a renormalized system Hamiltonian.



This figure plots, for a specific qutrit system, the trace distance between the SC equilibrium state proposed here and the numerically evaluated equilibrium state as a function of the coupling strength, for the model described by Eq. 8.

For a continous variable system with the system Hamiltonian given as $\hat{H}_S = \frac{\hat{p}^2}{2m} + V(\hat{q})$ and $\hat{A} \equiv \hat{q}$, the equilibrium state shows deviation from the harmonic environment case, and is given as,

$$\langle q|\rho_{SC}|q'\rangle = Z^{-1}\delta(q,q')\langle q|e^{-\beta\hat{H}_{\mathrm{eff}}}|q'\rangle, \tag{9}$$

$$\hat{H}_{\mathrm{eff}} = \frac{\hat{p}^2}{2M_{\mathrm{eff}}} + V_{\mathrm{eff}}(\hat{q}), \tag{10}$$

where, $M_{\mathrm{eff}} = m + \sum_k m_k$ and $V_{\mathrm{eff}}(x) = V(x) + \sum_{k=1}^{N} U_k^{\mathrm{free}}(x)$. We note that this converges to the harmonic environment result (Eq. 3) in the limit $M_{\mathrm{eff}} \to \infty$.

Intuitive Proof: The action corresponding to Eq. 8 is given as

$$S_k \equiv \int_0^\beta dt\left\{\frac{m_k}{2}\dot{q}_k(t)^2 + U_k^{\mathrm{free}}(q_k(t)) + \frac{\alpha_k}{2}U_k(q_k(t) - A(t))\right\}. \tag{11}$$

In the SC limit ($\alpha_k \to \infty$), for paths with non-negligible contribution, the condition $q_k(t) = A(t)$ and $A(0) = A(\beta)$ gets imposed. The action simplifies as

$$S_k[A(t)] = \int_0^\beta dt\left\{\frac{m_k}{2}\dot{A}(t)^2 + U_k^{\mathrm{free}}(A(t))\right\}. \tag{12}$$

Hence eliminating the path integral over the environment degrees of freedom and giving rise to the expression for the SC equilibrium state derived here.

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