Configurational Entropy and Adam-Gibbs Relation for Quantum Liquids

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I. LINEAR DEPENDENCE OF SHAPE FUNCTION ON THE INHERENT STRUCTURE ENERGY

In this section, we show that the shape function $\mathcal{S}(N, V, T, e_{IS})$ for the ring polymers systems, defined in Eq. 12 in the main manuscript, is a linear function of the inherent structure energy e_{IS} for all values of the quantumness h and for all temperatures T studied. In Fig. S1, we plot the shape function of the ring-polymers system as a function of the inherent structure energy for the LJBMs with Planck's constant h_a and h_c, at temperatures $T = 0.475, 0.8, 1.0$. The shape function at each point is computed from the IS normal mode frequencies of the classical system, using the method described in Ref. [1]. Solid lines are linear fits to the data points with $e_{IS} \leq -7.6$ (dashed line), above which the Gaussian and harmonic approximation of the PEL of the classical system is no longer valid; see also Fig. 2 of the main manuscript. From the linear fits in Fig. S1, we extract the fitting parameters $a(T)$ and $b(T)$ defined in Eq. 12 of the main manuscript.

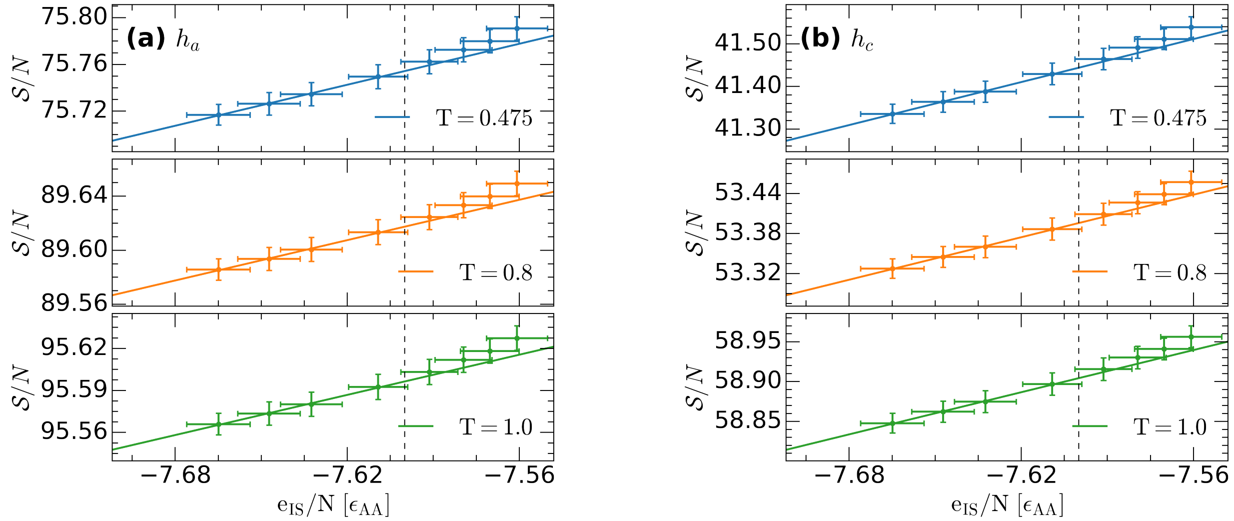

FIG. S1. Shape function of the ring-polymer system as a function of the inherent structure energy for the LJBMs with Planck's constant (a) $h = h_a$ and (b) $h = h_c$. Each panel includes data at three different temperatures. The solid lines are linear fits to the data points with $e_{IS} \leq -7.6$ (dashed line). The solid lines are linear fits to the data points for $e_{IS} < -7.6$, where the Gaussian and harmonic approximation of the classical PEL holds.

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II. THE IMPORTANCE OF ANHARMONIC CONTRIBUTIONS TO THE CONFIGURATIONAL ENTROPY

The configurational entropy, $S_{IS}(N,V,e_{IS})$, of the classical and quantum LJBMs is given by Eq. 10 (Gaussian approximation) and is shown in Fig. 5(a). In the main manuscript, this expression for $S_{IS}(N,V,e_{IS})$ (Eq. 10) is validated using Eq. 34 (or, equivalently, Eq. 33) including the anharmonic contributions to the Helmholtz free energy, $F_{vib}^{anh}(N,V,T)$. The agreement between Eq. 34 and Eq. 10 is remarkable (Fig. 6).

That anharmonic contributions for the PEL formalism ($F_{vib}^{anh}(N,V,T)$) are relevant for the quantum LJBMs studied is evident from Figs. 2(a) and 2(b) of the main manuscript. One may wonder, how relevant the anharmonic contributions are for the configurational entropy $S_{IS}(N,V,e_{IS})$ given in Eq. 10. To address this point, we test whether Eq. 34 holds when anharmonicities are removed [$F_{vib}^{anh}(N,V,T) \to 0$]. Specifically, here we test whether Eq. 10 satisfies the following expression,

$$S_{IS}(T,e_{IS})/k_B = \ln\left(\mathrm{P}(T,e_{IS})\right) + 3Nn_b \ln(\beta\hbar\omega_0) + \mathcal{S}(T,e_{IS}) + \beta e_{IS} + c(T) \qquad \text{(S1)}$$

As shown in Fig.S2, Eq. S1 is consistent with Eq. 10 for $h = 0, h_a$. However, a close comparison of Fig. S2 and Fig. 2(a)(b) of the main manuscript, shows that for $T = 1.0$ (orange circles), Eq. 34 works slightly better than Eq. S1. As the quantum character of the LJBMs increases, small deviations are observed at lower temperatures. While in Fig. 2(c) of the main manuscript the values of S_{IS} at $T = 0.65$ (blue triangles) obey Eq. 10 (black line), this is not the case when Eq. S1 is used [blue triangles and black line in Fig. S2(c)]. Despite the slightly better performance of Eq. 34, compared to Eq. S1, the anharmonic contributions to the S_{IS} of the LJBMs studied seem to be small for $h = 0, h_a, h_b, h_c$, but seem to become increasingly relevant as h further increases ($h > h_c$).

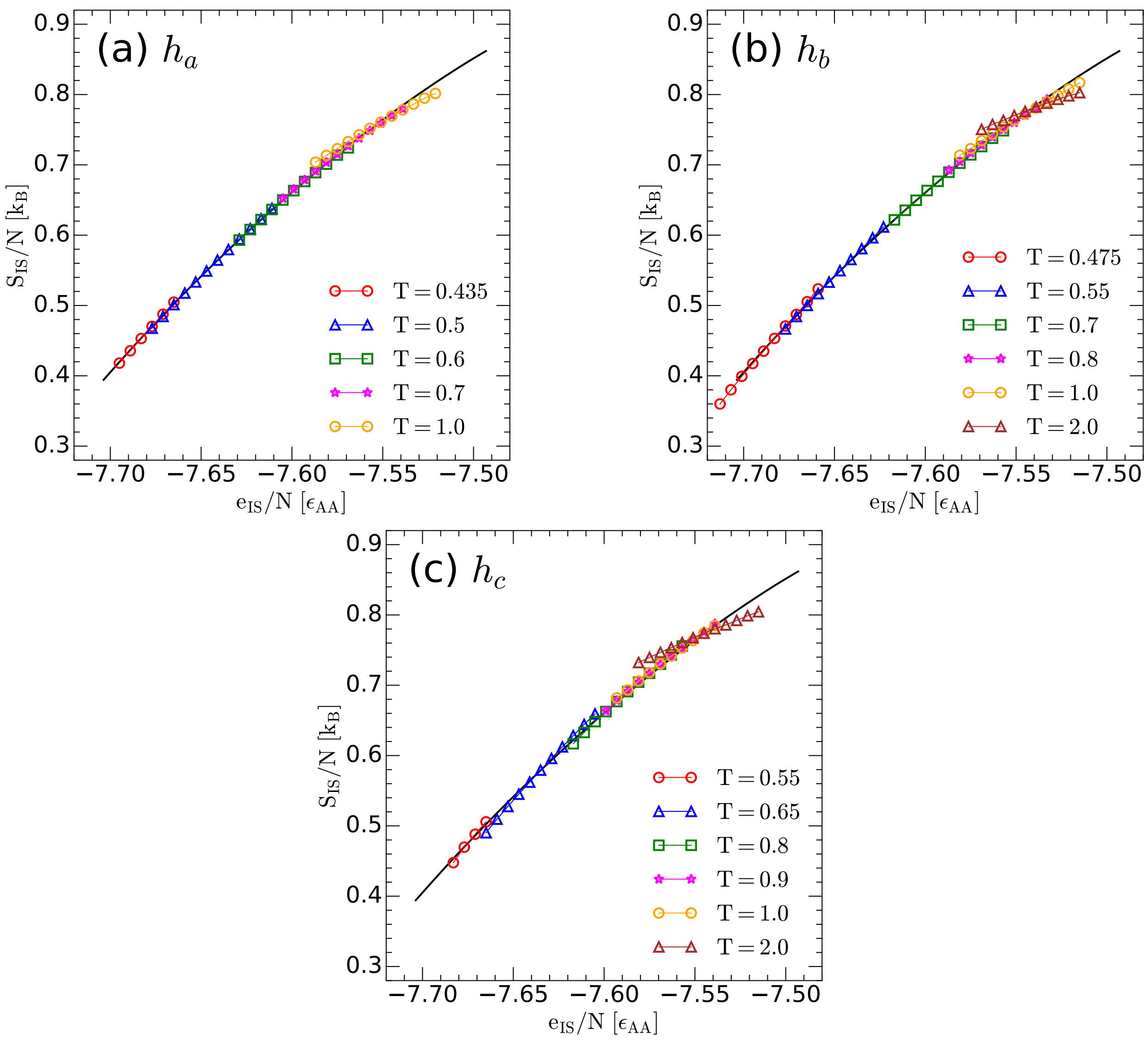

FIG. S2. (a) Configurational entropy of the LJBMs as a function of the IS energy e_{IS}, $S_{IS}(e_{IS})$ [solid black line; taken from Fig. 5(a) of the main manuscript]. The symbols correspond to the expression on the right-hand-side of Eq. S1 for temperatures $T = 0.435$ (red circles), 0.5 (blue up-triangles), 0.6 (green squares), 0.7 (magenta stars) and 1.0 (orange circles). Results at the different temperatures are obtained from ring-polymer molecular dynamics (RPMD) simulations with $h = h_a$ [datasets are shifted by a constant $c(T)$; see text]. (b) Same as (a) for $h = h_b$, and for temperatures $T = 0.475$ (red circles), 0.55 (blue up-triangles), 0.7 (green squares), 0.8 (magenta stars), 1.0 (orange circles), and 2.0 (maroon up-triangles). (c) Same as (a) for $h = h_c$, and for temperatures $T = 0.55$ (red circles), 0.65 (blue up-triangles), 0.8 (green squares), 0.9 (magenta stars), 1.0 (orange circles), and 2.0 (maroon up-triangles). In contrast to Fig. 6 of the main manuscript, the orange symbols in (a) and (b) [T=1.0] deviate slightly from the black line. Similarly, the blue triangles in (c) [T=0.65] deviate slightly from the black line.

[1] A. Eltareb, Y. Zhou, G. E. Lopez, and N. Giovambattista, Potential energy landscape formalism for quantum molecular liquids, Communications Chemistry **7**, 289 (2024).