

monic oscillator (SHO). The entropy S_{sho} of a one-dimensional simple harmonic oscillator can be expressed analytically as

$$S \leq S_{\text{sho}} = \frac{k_B \alpha}{e^\alpha - 1} - k_B \ln[1 - e^{-\alpha}], \quad (3)$$

where $\alpha = \hbar \omega / k_B T$, $\hbar = h/2\pi$, ω is the frequency of the oscillator, and h is Planck's constant. It was shown by Schlitter⁹ that the entropy of the harmonic oscillator S_{sho} is an upper bound for the *true* entropy S of the system.

The frequency ω of the oscillator depends on the quantum-mechanically defined variance $\langle x^2 \rangle$ and must be connected to the classical variance $\langle x^2 \rangle_c$ that can be measured in classical simulations. As a connection, the equipartition theorem

$$m \omega^2 \langle x^2 \rangle_c = k_B T \quad (4)$$

is used. The equipartition theorem holds only in the limit $\hbar \omega \ll k_B T$. This approximation is likely to be good because in a molecule the high-frequency motions for which it fails will contribute very little to the entropy.

In the generalization of the formula to many degrees of freedom it is simpler to use an approximation to Eq. (3) which was introduced and rationalized by Schlitter,⁹

$$S \leq S_{\text{sho}} < S' = \frac{1}{2} k_B \ln \left(1 + \frac{e^2}{\alpha^2} \right) \quad (5)$$

$$= \frac{1}{2} k_B \ln \left(1 + \frac{k_B T e^2}{\hbar^2} m \langle x^2 \rangle_c \right). \quad (6)$$

Here $e = \exp(1)$ is Euler's number.

A. Many degrees of freedom

The generalization to many degrees of freedom is based on the covariance matrix σ of the atom-positional fluctuations with the elements

$$\sigma_{ij} = \langle (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \rangle, \quad (7)$$

where x_1, \dots, x_{3N} are the Cartesian coordinates of an N particle system. The covariance matrix can also be expressed in mass-weighted coordinates $x'_i = x_i / \sqrt{m_i}$ and becomes

$$\sigma' = \mathbf{M}^{1/2} \sigma \mathbf{M}^{1/2} = \mathbf{M} \sigma, \quad (8)$$

where $\mathbf{M} = \mathbf{M}^{1/2} \mathbf{M}^{1/2}$ is the mass matrix of rank $3N$ in which the diagonal elements hold the masses and $m_{ij} = 0$ for $i \neq j$. The last identity holds because σ and $\mathbf{M}^{1/2}$ are both symmetric matrices.

The mass-weighted covariance matrix can be diagonalized, giving a new set of *uncorrelated* (the off-diagonal elements are 0) coordinates q_i . For each of these new degrees of freedom the entropy can be calculated with Eq. (6) and the variances $\langle q_{ii}^2 \rangle_c$ which are the diagonal elements of the matrix σ' (expressed in the coordinates q_i),

$$\begin{aligned} S < S' &= \frac{1}{2} k_B \sum_{i=1}^{3N} \ln \left[1 + \frac{k_B T e^2}{\hbar^2} \langle q_{ii}^2 \rangle_c \right] \\ &= \frac{1}{2} k_B \ln \left(\prod_{i=1}^{3N} \left[1 + \frac{k_B T e^2}{\hbar^2} \langle q_{ii}^2 \rangle_c \right] \right). \end{aligned} \quad (9)$$

Taking the product of the diagonal elements of a diagonal matrix as in Eq. (9) is equivalent to calculating the determinant of the matrix σ' . Because the determinant of a matrix is invariant under any orthogonal transformation Eq. (9) can be rewritten as⁹

$$S' = \frac{1}{2} k_B \ln \det \left[\mathbf{1} + \frac{k_B T e^2}{\hbar^2} \mathbf{M} \sigma \right]. \quad (10)$$

Therefore, the transformation to an internal, non-Cartesian set of coordinates is not necessary. To calculate the entropy using Eq. (10), it is only necessary to calculate the covariance matrix [Eq. (7)] from a trajectory. The correct quantum-mechanical limit for high-frequency motion is obtained with Eq. (10), because a covariance matrix whose elements are all vanishingly small will give an entropy of zero.

Very slow motions like the center of mass motion of a larger molecule can lead to a constantly increasing variance and therefore to a convergence problem in the entropy calculations based on Eq. (10). A simple translational fit on the centers of mass of the molecules at the various time points, however, will remove the center of mass motion and lead to more rapidly converging results. The missing entropy contribution (the ideal gas contribution) can be calculated analytically, if required.

B. Approximations

Several approximations are used in the derivation of the formula described above:

- (1) Every degree of freedom is treated as a quantum harmonic oscillator,
- (2) The equipartition theorem is used to connect the classical variance and the frequency of a quantum harmonic oscillator [Eq. (4)], and
- (3) An approximate expression [Eq. (5)] for the entropy of a quantum harmonic oscillator is used.

As stated above, the second approximation is not expected to give rise to any significant errors, as high-frequency motions will contribute little to the entropy. The third approximation can also be shown to be very good over the whole range of molecular frequencies ω .⁹

The first approximation might break down depending on the type of system that is examined. Bond vibrations, angle-bending, and torsional-angle motions in a molecule are probably well described by a harmonic approximation. The motion of a molecule inside a solvent, on the other hand, is probably a bad case for an harmonic approximation. Section IV B examines these effects in detail for the entropy of a Lennard-Jones fluid.

III. STOCHASTIC DYNAMICS OF HARMONIC OSCILLATORS

The simplest system to test Schlitter's formula is an ensemble of independent classical harmonic oscillators. The results can be calculated analytically and checked against the results from simulations.

One hundred completely independent, noninteracting particles of mass 15.994 amu were harmonically restrained