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An improved thermodynamic energy estimator for path integral simulations

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A new path integral energy estimator is presented that improves upon the thermodynamic energy estimator via a free particle projection. This centroid thermodynamic estimator significantly reduces the numerical noise of the thermodynamic estimator. The debate as to which estimator is better (virial, centroid virial, or thermodynamic) is partially resolved. The centroid estimators are found to be significantly better than their noncentroid analogues. The new centroid thermodynamic estimator has accuracy close to the centroid virial estimator, and may have particular advantages when derivatives of the potential are expensive to evaluate. © *2002 American Institute of Physics.*
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I. INTRODUCTION

The path integral Monte Carlo[1–3] (PIMC) method has found wide application in quantum physics[4] and chemistry.[5] We consider here a non-relativistic particle of mass m, temperature T, and Hamiltonian $H=p^2/2m+V$ in one spatial dimension. The equations are generalizable to multiple particles in multiple dimensions, either distinguishable or with exchange statistics. We define $\beta\equiv 1/k_B T$, where k_B is Boltzmann's constant. In the path integral technique, the canonical density matrix $\rho(r_1,r_1',\beta)=\langle r_1|e^{-\beta H}|r_1'\rangle$ is evaluated by inserting $N-1$ resolutions of the identity:

$$\rho(r_1,r_{N+1},\beta)=\int dr_2\cdots dr_N\prod_{j=1}^{N}\rho(r_j,r_{j+1},\beta/N). \quad (1)$$

Since the density matrices in the integrand are evaluated at temperature NT, a high temperature Trotter approximation is valid:[6]

$$\rho(r_j,r_{j+1},\beta/N)\approx\left(\frac{Nm}{2\pi\hbar^2\beta}\right)^{1/2}\exp\left\{-\frac{Nm}{2\hbar^2\beta}(r_j-r_{j+1})^2 - \frac{\beta}{2N}[V(r_j)+V(r_{j+1})]\right\}. \quad (2)$$

The path integral approach to the density matrix is applicable to the canonical partition function $Q\equiv\int dr\rho(r,r,\beta)$, given by

$$Q=\left(\frac{Nm}{2\pi\hbar^2\beta}\right)^{N/2}\int dr_1\cdots dr_N e^{-\beta V_C}, \quad (3)$$

where the propagator potential V_C is defined by

$$V_C\equiv\sum_{j=1}^{N}\left[\frac{Nm}{2\hbar^2\beta^2}(r_j-r_{j+1})^2+\frac{1}{N}V(r_j)\right], \quad (4)$$

with $r_{N+1}\equiv r_1$. Equation (4) leads to the well-known interpretation that the quantum path integral is the same as a classical expectation value of the chain potential V_C, which consists of N beads bound together by harmonic interactions and acting with an external potential V. V_C is called the primitive propagator because it is valid to first order in $Nm/\hbar^2\beta$.

II. CURRENTLY USED ENERGY ESTIMATORS

In the present work we consider calculating the expectation value of the quantum mechanical energy E. The most straightforward method[7] is differentiating $E\equiv-\partial\ln Q/\partial\beta$:

$$E=\frac{1}{Q}\left(\frac{Nm}{2\pi\hbar^2\beta}\right)^{N/2}\int dr_1\cdots dr_N\epsilon_T e^{-\beta V_C}, \quad (5)$$

where

$$\epsilon_T=K_T+\overline{V}, \quad (6)$$

$$\overline{V}=\frac{1}{N}\sum_{j=1}^{N}V(r_j), \quad (7)$$

$$K_T=\frac{N}{2\beta}-\frac{Nm}{2\hbar^2\beta^2}\sum_{j=1}^{N}(r_j-r_{j+1})^2. \quad (8)$$

Equation (5) can be evaluated via the Metropolis Monte Carlo method.[8] ϵ_T is called the thermodynamic estimator for E when $r_1\cdots r_N$ are sampled according to V_C. ϵ_T is also known as the Barker estimator.

The ϵ_T approach to E can be problematic in practice. The mean square fluctuations in ϵ_T grow as $N/2\beta^2$ (hence, with the accuracy),[9] suggesting that the virial estimator $\epsilon_V=K_V+\overline{V}$ is better behaved:[9–12]

$$K_V=\frac{1}{2N}\sum_{j=1}^{N}r_jV'(r_j). \quad (9)$$

A constant boundary term is sometimes added to properly treat the transformation of the integral to the virial form, depending upon the values of V and ρ at the system boundaries.[13] The centroid virial estimator $\epsilon_{CV}=K_{CV}+\overline{V}$ has been suggested, although the distinction between ϵ_V and ϵ_{CV} is often ignored.[4]

$$K_{CV}=\frac{1}{2\beta}+\frac{1}{2N}\sum_{j=1}^{N} y_j V'(r_j), \tag{10}$$

where $y_j \equiv r_j - q$ and q is the centroid variable $q \equiv (1/N)\sum_{j=1}^{N} r_j$. The stretch estimator, the diffusion estimator, and directly applying H to ρ have been proposed, but all have difficulties in usability.[4,14] There is an unresolved debate as to which estimator is better depending upon what sampling method is used and what chemical system is studied (with some authors changing sides).[4,5,7,9–20]

There are practical considerations that favor ϵ_T. Calculating K_T requires one less order of derivative information than K_V or K_{CV} for a given propagator. For example, ϵ_T when used with the higher order propagator (see below) requires only V', whereas ϵ_V and ϵ_{CV} require V''. This is problematic in *ab initio* path integral methods where V is computed via an electronic structure method, since V'' is often computationally expensive or unavailable. Also, for some *ab initio* methods, V' can cost easily an order of magnitude more than V, eliminating the speedup gained by choosing a virial based estimator. Partial averaged Fourier PIMC requires derivatives one higher than the higher order propagator.[21] This is particularly important as *ab initio* path integrals begin to appear in the literature.[22–26]

Higher order approximations (in $\hbar^2\beta/Nm$) to the density matrix have been shown to significantly increase the rate of convergence as a function of N.[27–30] These methods are important when the tools available for two-body interactions[4] are not applicable, such as in *ab initio* path integrals. The next higher order propagator replaces V in Eq. (4) with $V_{\text{eff}}(r)=V(r)+\beta^2\hbar^2[\nabla V(r)]^2/24N^2m$, where the second term is the quantum correction to V.[31–33] Higher order energy estimators $(\epsilon_T^{(2)},\epsilon_V^{(2)},\epsilon_{CV}^{(2)})$ may also be derived for this density matrix, where the derivation is completely analogous to the one presented above.[34] We should note that for large $\hbar^2\beta/Nm$, V_{eff} may be problematic.[35,36]

III. THE CENTROID THERMODYNAMIC ENERGY ESTIMATOR

We now show that the fluctuations of ϵ_T can be reduced without significant computational overhead. In this method, we seek a function f whose expectation value $\langle f\rangle$ is known or readily calculated. We then calculate a new correlated estimator $\epsilon_T - f$, with expectation value of $E-\langle f\rangle$. If the covariance $\langle \epsilon_T f\rangle$ is sufficiently large, the variance of the new estimator will be significantly less than that of ϵ_T. The growing fluctuations come from the Brownian motion of the free particle part of the problem, suggesting the free particle energy as a correlated estimator,

$$\frac{1}{2\beta}=\int dr_1\cdots dr_N K_T(r_1\cdots r_N)e^{-\beta V_{\text{fp}}(r_1\cdots r_N)} \times\left(\int dr_1\cdots dr_N e^{-\beta V_{\text{fp}}(r_1\cdots r_N)}\right)^{-1}, \tag{11}$$

where V_{fp} is defined by Eq. (4), but with $V\equiv 0$. $\epsilon_T \equiv K_T$ for the free particle, because $V\equiv 0$. The free particle energy's independence of the centroid variable q may be demonstrated by a simple change of variables and using the relation $y_N=-\sum_{i=1}^{N-1} y_i$. We then have (with $d\mathcal{X}\equiv dy_1\cdots dy_{N-1}dq$)

$$\frac{1}{2\beta}=\int d\mathcal{X} K_T(y_1\cdots y_N)e^{-\beta V_{\text{fp}}(y_1\cdots y_N)} \times\left(\int d\mathcal{X} e^{-\beta V_{\text{fp}}(y_1\cdots y_N)}\right)^{-1}. \tag{12}$$

The integrals in Eq. (12) are independent of q, allowing us to arbitrarily choose a weighting function based on q. Weighting by $e^{-\beta V(q)}$ will dramatically increase the covariance of the free particle energy estimator with the total energy estimator ϵ_T (failing to apply this weight makes the method ineffective). Thus, we have

$$\frac{1}{2\beta}=\int d\mathcal{X} K_T(y_1\cdots y_N)e^{-\beta V_{\text{fp}}(y_1\cdots y_N)-\beta V(q)} \times\left(\int d\mathcal{X} e^{-\beta V_{\text{fp}}(y_1\cdots y_N)-\beta V(q)}\right)^{-1}. \tag{13}$$

Our next objective is to transform Eq. (13) so that it has the same Boltzmann factor as Eq. (5). This is accomplished using the umbrella sampling scheme:[37] $\langle G\rangle_2 = \langle G e^{-\beta\Delta V}\rangle_1 / \langle e^{-\beta\Delta V}\rangle_1$, where $\langle O\rangle_j$ denotes the classical expectation value of O according to potential j and $\Delta V = V_2 - V_1$. In our case, $V_2 = V_{fp} + V(q)$, $V_1 = V_C$, $G = K_T$, and $\langle G\rangle_2 = 1/2\beta$ leads to

$$\frac{\langle e^{-\beta\Delta V}\rangle_1}{2\beta}=\langle K_T e^{-\beta\Delta V}\rangle_1. \tag{14}$$

For multiple particles in multiple dimensions, the $1/2\beta$ is simply replaced with $MD/2\beta$, where M is the number of atoms and D is the number of dimensions. Thus we choose

$$f=K_T e^{-\beta\Delta V}. \tag{15}$$

The integral of f can be evaluated at the end of a Monte Carlo calculation provided that we determine the normalization factor $\langle e^{-\beta\Delta V}\rangle_1$ as part of the Monte Carlo calculation.

We expect that in the $\hbar^2\beta/Nm \ll 1$ limit, the quantum centroid will collapse and ϵ_T will become highly correlated with f. In the low T limit, f may lose correlation with ϵ_T, suggesting that we use $\epsilon_T - \alpha f$ with α chosen to minimize the variance. A derivation similar to the one in Ref. 12 shows that the optimal α is

$$\alpha=\frac{\langle \epsilon_T f\rangle - \langle \epsilon_T\rangle\langle f\rangle}{\langle f^2\rangle - \langle f\rangle^2}. \tag{16}$$

The variance of $\epsilon_T - \alpha f$ is always less than that of ϵ_T by a factor of $\alpha(\langle \epsilon_T f\rangle - \langle \epsilon_T\rangle\langle f\rangle)$.

Let us summarize the resulting algorithm. We conduct a Monte Carlo calculation using the potential V_C and accumulate the averages of estimators ϵ_T and f, normalization factor $\langle e^{-\beta\Delta V}\rangle$, and covariances $\langle \epsilon_T f\rangle$ and $\langle f^2\rangle$. By using the normal modes of the chains as the Monte Carlo variables efficiency is gained because $V(q)$ rarely changes.[38] At the end of the calculation, we determine α. The quantum mechanical energy is then given by

$$E=\langle \epsilon_T\rangle - \alpha\langle f\rangle + \alpha\langle e^{-\beta\Delta V}\rangle/2\beta. \tag{17}$$

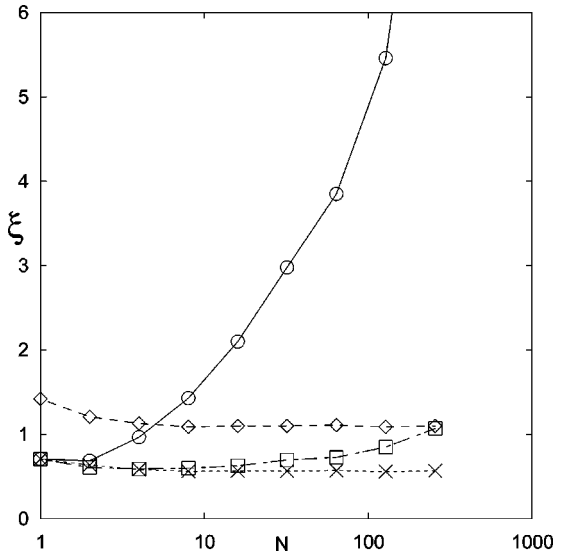

FIG. 1. The normalized fluctuations of the energy estimator (ξ) for the harmonic oscillator with $k_BT/\hbar\omega=0.05$ as a functions of beads, N. The symbols in all figures are $\bigcirc\equiv\epsilon_T$, $\square\equiv\epsilon_{CT}$, $\diamond\equiv\epsilon_V$, and $\times\equiv\epsilon_{CV}$.

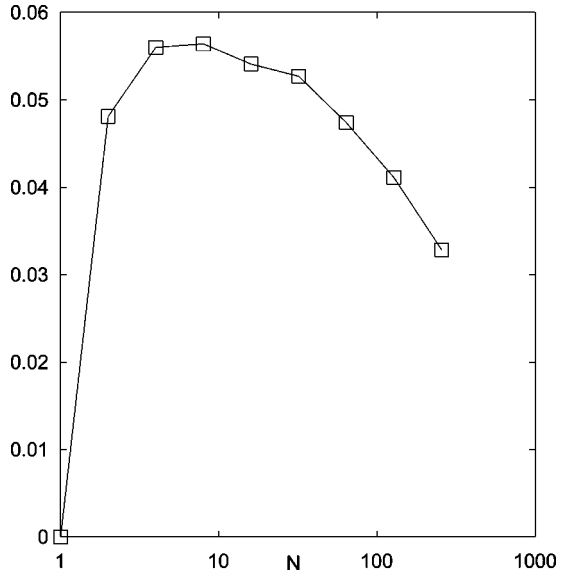

FIG. 2. The standard deviation of $\alpha\langle e^{-\beta\Delta V}\rangle/2\beta$ divided by standard deviation of ϵ_{CT}, for the system in Fig. 1.

This correction is independent of the sampling scheme: normal modes, primitive, PIMD, etc.[4,5] A similar correction is likely derivable for noncanonical ensembles.[39–41] The new estimator is called ''centroid thermodynamic'' ϵ_{CT}, due to its deviation from ϵ_T by a centroid projection. Attempts to apply this projection to ϵ_V and ϵ_{CV} failed to change the variance in all systems studied and therefore no results for those methods are presented. The method is summarized in the Appendix.

IV. RESULTS

We define $\xi=|\sigma/E|$ to be a normalized measure of fluctuations to compare the stabilities of the estimators, where σ^2 is the variance of the given energy estimator. A comparison of the estimators using the harmonic oscillator, $V=m\omega^2x^2/2$, is presented in Fig. 1 with $k_BT/\hbar\omega=0.05$. In these calculations, normal mode sampling was used with the primitive propagator. The number of Monte Carlo cycles was chosen to converge the value of ξ. The variances shown are independent of sampling scheme. As expected, the divergence of ϵ_T increases with N. For ϵ_{CT}, α increases with N and cancels out significant portions of the divergence. ϵ_{CV} is clearly superior to ϵ_V, and some of the reported deficiencies of ϵ_V are significantly reduced by using ϵ_{CV}. In Fig. 2, the standard deviation of $\alpha\langle e^{-\beta\Delta V}\rangle/2\beta$ divided by the standard deviation of ϵ_{CT} is plotted. The noise in the normalization term $\langle e^{-\beta\Delta V}\rangle$ is clearly small compared to that of E. Therefore the noise in E is not simply being moved over into the normalization term. This is expected since most of the noise comes from K_T and not V.

Our new method was also applied to Lennard-Jones clusters of Ar_6 in Figs. 3–5 ($\sigma=6.435$ a.u., $\epsilon/k_B=119.8$ K).[42] At all T studied, ϵ_V (but not ϵ_{CV}) performs poorly. This is because ϵ_{CV} eliminates the divergent behavior found in ϵ_V as the interatomic distance goes to zero found in previous work,[19] because the r in Eq. (9) is replaced with y in Eq. (10). At 0.5 K, ϵ_{CT} and ϵ_T are indistinguishable as is expected (highly quantum, $\alpha\approx0$). As N increases, ϵ_{CV} replaces ϵ_{CT} as the better estimator. At 15 K, the α factor provides a correction and ϵ_{CT} is better than ϵ_T. Although this improvement is marginal and ϵ_{CV} is still better than ϵ_{CT} at 15 K, the improvement is significant because computational work is proportional to the deviation squared and ϵ_{CT} does not require knowledge of V'. As T rises to 50 K, ϵ_T suffers from a large divergence, but ϵ_{CT} and ϵ_{CV} perform well. The best estimator clearly depends upon the specific conditions. For small NT (large $\hbar^2\beta/Nm$) the thermodynamic estimators ϵ_T and ϵ_{CT} are best. For large NT the centroid estimators ϵ_{CV} and ϵ_{CT} are best, because as the system heats up, the chain collapses to the centroid. For small N, ϵ_V is the worst because it has no classical $1/2\beta$ type term. Clearly, ϵ_{CV} and ϵ_{CT} are the better estimators.

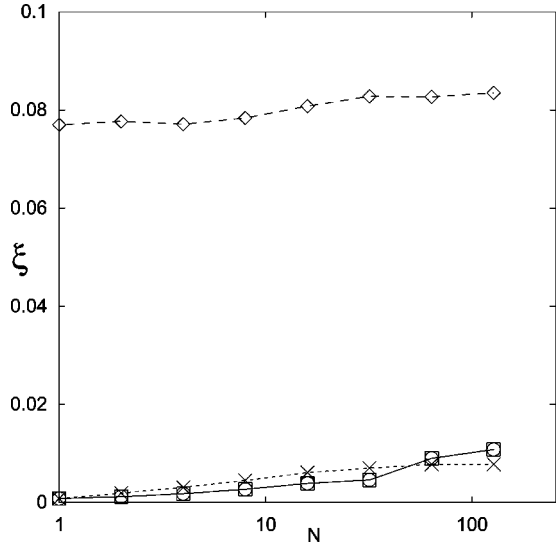

FIG. 3. Ar_6 at 0.5 K, symbols as in Fig. 1.

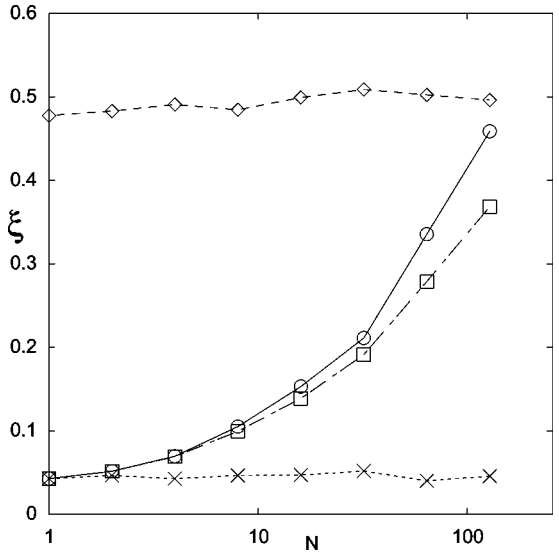

FIG. 4. Ar_6 at 15 K; symbols as in Fig. 1.

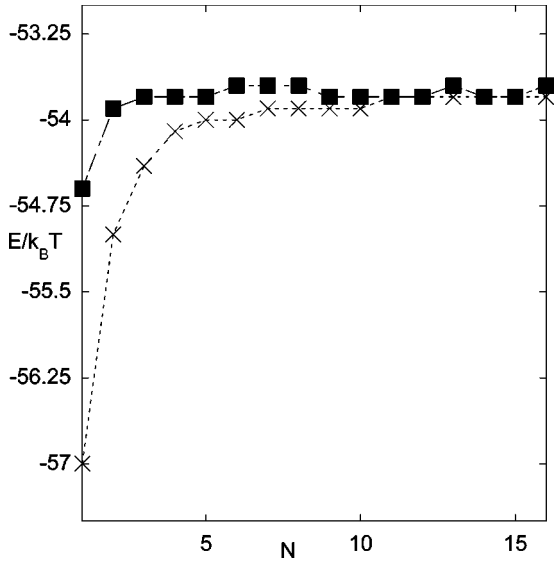

FIG. 6. Ar_6 at 20 K. The filled boxes are $\epsilon_{CT}^{(2)}$ and crosses are ϵ_{CV}.

Assuming that we have only V and V', but not V'' (often the case), we can use $\epsilon_{CT}^{(2)}$ but not $\epsilon_{CV}^{(2)}$. Therefore, because $\epsilon_{CT}^{(2)}$ requires fewer beads than ϵ_{CV}, the computational requirements could be less for $\epsilon_{CT}^{(2)}$. We compare $\epsilon_{CT}^{(2)}$ and ϵ_{CV} for Ar_6 at 20 K in Fig. 6. To achieve the accuracy of $\epsilon_{CT}^{(2)}$ with 1, 2, and 3 beads, using ϵ_{CV} requires 3, 6, and 11 beads, respectively. In each case we find that the deviation is larger for ϵ_{CV} than for the equivalently accurate $\epsilon_{CT}^{(2)}$. The ϵ_{CV} calculation will be longer than the equivalent $\epsilon_{CT}^{(2)}$ calculation by a factor 4.6 for 3 beads, 3.4 for 6 beads, and 4.7 for 11 beads. In calculating these factors, the increased autocorrelation time with N, the increased number of V evaluations needed per Monte Carlo step with N, and the evaluations of $V(q)$ are all taken into account.

The centroid thermodynamic energy estimator may be particularly advantageous when V' is unavailable or expensive to calculate. This occurs when V' is calculated with high level electronic structure methods such as many body perturbation theory. As an example, we studied the ion radical $\cdot CH_2^+$. The classical potential V was calculated with the 6-311G** basis set[43] and unrestricted[44] second order many body perturbation theory using the GAMESS code.[45] At 2000 K with 16 beads the variance of the mean is 10.1 kcal/mol for ϵ_T and 0.8 kcal/mol for ϵ_{CT}. This results in a 160-fold reduction in the number of Monte Carlo steps needed to calculate the energy. For 1000 K the step reduction is 55%, while with 32 beads the reduction is 60%. For 300 K the step number reduction is 5%.

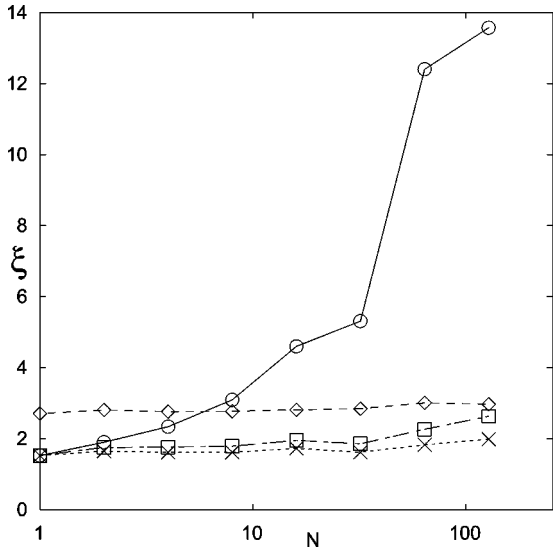

FIG. 5. Ar_6 at 50 K, symbols as in Fig. 1.

V. CONCLUSIONS

We have presented a new estimator based on umbrella sampling to significantly improve the efficiency of path integral energy calculations. Our proposed centroid thermodynamic estimator (ϵ_{CT}) has smaller fluctuations than the thermodynamic estimator ϵ_T. We have applied ϵ_{CT} to analytic potentials and potentials based on *ab initio* electronic structure. We have found that the centroid virial estimator ϵ_{CV} has smaller fluctuations than the virial estimator ϵ_V. At low NT, ϵ_{CT} has smaller fluctuations than ϵ_{CV}. ϵ_{CT} also has advantages at higher NT because it requires one less derivative of the potential than ϵ_{CV}. There is an intermediate regime (Ar_6 at 15 K) where ϵ_{CV} is better, because T is large enough that ϵ_T is noisy, but T is not large enough for the free particle projection to be more than marginally better. The free particle projections presented may be applicable to other properties calculated via estimators, such as pressure and heat capacity. An energy estimator based on a linear combination of ϵ_T, f, and ϵ_{CV} would provide the optimal energy estimator in all cases, with only a little more work than that of ϵ_{CV}. This estimator would minimize the numerical noise.

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APPENDIX: SUMMARY OF METHODOLOGY

- Loop over normal modes.
  - Attempt a Monte Carlo step.
  - If move is accepted then,
    * If mode is the centroid motion calculate $V(q)$.
    * Calculate K_T, V_{fp}, V_C, ΔV.
  - End if.
  - Accumulate f, ϵ_T, $e^{-\beta\Delta V}$.
- End loop.
- Calculate optimal α with Eq. (16).
- Calculate corrected E with Eq. (17).

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