Free Energy Perturbation Theory at Low Temperature

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The perturbative expansion introduced by Zwanzig [R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954)] expresses the difference in Helmholtz free energy between a system of interest and that of a reference system as series of cumulants $\kappa_n$ of the potential energy difference between the two systems. This expansion has attractive features as a method for obtaining absolute free energies for ab initio potential energy surfaces. The series is formally a power series in $\beta = 1/T$, suggesting that its usefulness may be limited to high temperature. However, for smooth reference potentials, the $T$-dependence of the $\kappa_n$ contributes to the convergence. A closed form expression is derived for the $\kappa_n$ to all orders for the case that both the system and reference potentials are harmonic. In this case $\kappa_n \propto T^n$ for $n \geq 2$ and the convergence of the series is independent of temperature. More realistic cases of liquid Cu and solid Al, with a $1/r^{12}$ and harmonic reference potential, respectively, are investigated numerically by evaluating the cumulants to third order using Monte Carlo integration. In all cases, the ratio of the third order to the second order term in the expansion is found to be $\sim 0.1$, indicating good convergence. Third order contributions to the free energy are typically a few meV/atom, and comparable to their statistical errors. The statistical error in the second order free energy of Al is 0.4 meV/atom with only 100 evaluations of the ab initio energy. These results suggest that the perturbation series allows for efficient and accurate evaluation of the free energy for condensed phases.

I. INTRODUCTION

Standard methods for determining the free energy for a given potential energy surface include thermodynamic and coupling constant integration [1, 2], umbrella sampling [3] and related generalized ensemble methods [4, 5]. The present work is motivated by the pursuit of efficient methods for determining bulk free energies of substances from ab initio potential energy surfaces. Classical statistical errors will be considered here, as is appropriate for liquids and anharmonic solids, except for the lightest elements. Standard methods may not be well suited to this application because they require a large number of evaluations of the expensive ab initio energy. The perturbative expansion due to Zwanzig [6] expresses the Helmholtz free energy $F$ of the system of interest, with potential energy function $U$, with respect to that of a known reference system with potential energy $U_0$,

$$\Delta F = F - F_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^{n-1}}{n!} \kappa_n$$  \hspace{1cm} (1)

where $\beta$ is the inverse temperature and the $\kappa_n$ are cumulants of the potential energy difference $\Delta U = U - U_0$. Units where Boltzmann’s constant $k_B = 1$ will be used in the formulae that follow. Results and figures will use conventional temperature units. The first few of these cumulants are

$$\kappa_1 = \langle \Delta U \rangle_0$$
$$\kappa_2 = \langle \Delta U^2 \rangle_0 - \langle \Delta U \rangle_0^2$$
$$\kappa_3 = \langle \Delta U^3 \rangle_0 - 3 \langle \Delta U \rangle_0 \langle \Delta U^2 \rangle_0 + 2 \langle \Delta U \rangle_0^3,$$  \hspace{1cm} (2)

where the notation $\langle \rangle_0$ denotes an expectation value in the canonical ensemble of the reference system. This expansion has some advantageous properties for the present application. Ensemble averages in the reference canonical ensemble can be computed by Monte Carlo sampling of the reference potential, which may be a simple pair potential, or similar model, and thus be orders of magnitude faster to evaluate than the ab initio potential. Equilibration and the generation of statistically independent configurations is carried out on the fast reference potential, and ab initio energies evaluated only for a greatly reduced set of configurations. Further gains in statistical efficiency result from the correlated fluctuations of the reference and system potentials, which reduce the statistical errors in the dominant first order term.

Some earlier findings indicating the promise of the approach include an investigation of liquid Cu represented by an embedded atom model (EAM) potential [7], with a $1/r^{12}$ potential as the reference. There it was found that the series truncated at second order has errors $< 1$ meV/atom without extensive fine-tuning of the reference potential. Statistical errors of a few meV/atom were obtained with 100 samples. In another work, ab initio energies were used for liquid Mg at ambient melting conditions [8]. The excess entropy obtained at second order was $-3.18(15)k_B/\text{atom}$ (the number in parenthesis denotes the one standard deviation statistical error in the final digits), compared to an experimental value of $-3.37k_B/\text{atom}$.

Due to the factors $\beta^{n-1}$ in the series Eq. (1), the expansion is usually called a high-temperature series [6, 8, 9, 10]. Zwanzig included this phrase in the title of his paper [6]. It might be expected that at low temperatures, truncating the series would lead to large errors, and its application to condensed phases would be suspect.

In the case of a hard sphere reference potential, the cumulants are temperature-independent and the series, Eq. (1) is indeed a high-temperature expansion. While
the hard sphere reference system has played a historically important role in the theory of liquids [9, 11, 12], it has no particular advantage for the applications of interest here. For more realistic, smooth reference potentials, the $\kappa_n$ will depend on $T$, and this dependence, together with the $\beta^{n-1}$ factors will determine the temperature behavior of the series. To the extent that $\kappa_{n+1}/\kappa_n \propto T$, the convergence of the series is independent of $T$. Dimensional analysis suggests $\kappa_n \propto T^n$.

The rest of this paper explores role of temperature in the convergence of the free energy perturbation series, Eq. (11) for condensed phases with smooth reference potentials. The first case considered is where both the system and reference potentials are harmonic. In this case, a closed form expression can be derived for $\kappa_n$, and it is found that $\kappa_n \propto T^n$ for $n \geq 2$ and the convergence of the series is independent of $T$. Truncation of the series results in a temperature-independent error in the entropy. Subsequently, two more realistic cases are considered. The $\kappa_n$ for $n \leq 3$ are evaluated numerically by Monte Carlo sampling of the reference canonical distribution. The first is a model of liquid Cu, represented by an EAM potential [13], with a $1/r^{12}$ pair potential as the reference system. It is found that with fixed reference potential strength, the convergence of the series gets worse with increasing temperature, while with the reference potential optimized at each temperature, the convergence is nearly independent of $T$. The final example is that of fcc Al with DFT energies and a harmonic reference potential. In this case, the ratio of the third order to the second order term in the free energy expansion is found to vary from 0.13 (39) at 300 K to 0.04 (28) at 900 K, again suggesting good convergence at low temperature.

II. CUMULANT EXPANSION

Some further properties of the expansion, Eq. (11) will be used in the following. The first is that under a constant shift $\Delta U \rightarrow \Delta U + c$, $\kappa_1 \rightarrow \kappa_1 + c$ while all $\kappa_n$ for $n > 1$ are unchanged. In applications, there are often large offsets between the system and reference potentials due to different zero energy states. This property means that these offsets are accounted for by the first order term in the series. The second property of interest is the variational property [11, 12] of the first order approximation

$$F_1 = F_0 + \langle \Delta U \rangle_0 \geq F$$

which allows optimization of the reference potential by minimizing $F_1$.

III. HARMONIC CASE

Consider the case where both the system and the reference are harmonic

$$U = \phi + \frac{1}{2} \mathbf{u}^T \mathbf{M} \mathbf{u}$$

$$U_0 = \phi_0 + \frac{1}{2} \mathbf{u}_0^T \mathbf{M}_0 \mathbf{u}_0$$

where $\mathbf{u}$ is a 3N-dimensional displacement vector from the local potential minimum, whose energy is $\phi$. The matrices $\mathbf{M}$ and $\mathbf{M}_0$ are symmetric and positive definite. They are not assumed to commute. This model is of interest as a realistic approximation for solids.

There are a number of ways to show that for this harmonic case, the cumulants $\kappa_n \propto T^n$ to all orders. It turns out to be possible to work out a closed form expression for the full expansion. Starting from the free energy difference in terms of the partition function, we have,

$$\Delta F = -T \ln \int \mathcal{D}\mathbf{u} \exp \left\{ -\beta \left( \phi + \frac{1}{2} \mathbf{u}^T \mathbf{M} \mathbf{u} \right) \right\}$$

Using a standard result for Gaussian integrals [14], this is

$$\Delta F = -\phi - \phi_0 + \frac{T}{2} \ln \left( \frac{\det (\mathbf{M})}{\det (\mathbf{M}_0)} \right)$$

$$= \phi - \phi_0 + \frac{T}{2} \ln \left( 1 + M_0^{-1/2} \Delta \mathbf{M} M_0^{-1/2} \right)$$

where $\Delta \mathbf{M} = \mathbf{M} - \mathbf{M}_0$. Then we can use the identity

$$\ln \det (\mathbf{A}) = \text{Tr} \ln (\mathbf{A})$$

to write

$$\Delta F = \phi - \phi_0 + \frac{T}{2} \text{Tr} \ln \left( 1 + M_0^{-1/2} \Delta \mathbf{M} M_0^{-1/2} \right)$$

Finally, expanding the logarithm, we have

$$\Delta F = \phi - \phi_0 + \frac{T}{2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \text{Tr} \left[ \left( M_0^{-1/2} \Delta \mathbf{M} M_0^{-1/2} \right)^n \right]$$

$$= \phi - \phi_0 + \frac{T}{2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \text{Tr} \left[ \left( M_0^{-1} \Delta \mathbf{M} \right)^n \right]$$

Eq. (8) is an expansion of $\Delta F$ in powers of $\Delta U \propto \Delta \mathbf{M}$, and is therefore equivalent to Eq. (11) for the harmonic case. It is straightforward to check that a direct evaluation of the first few orders with the formulae Eqs. (2) yields the same results as Eq. (8). So, by comparison of Eq. (8) to Eq. (11), we can read off,

$$\kappa_1 = \phi - \phi_0 + \frac{T}{2} \text{Tr} (M_0^{-1} \Delta \mathbf{M})$$

$$\kappa_n = \frac{T^n (n-1)!}{2} \text{Tr} \left[ \left( M_0^{-1} \Delta \mathbf{M} \right)^n \right], \ n \geq 2$$

(9)
The first cumulant incorporates the constant shift \( \phi - \phi_0 \) as well as a term \( \propto T \), while the higher cumulants have \( \kappa_n \propto T^n \). The temperature factors out of the series in Eq. \( \text{(8)} \) so \( T \) does not enter into its convergence at all. Convergence of the series requires that the eigenvalues \( \lambda_i \) of the matrix \( M_0^{-1} \Delta M \) satisfy \(-1 < \lambda_i \leq 1\), and is thus contingent only on properties of the reference and system potential surfaces. Truncation of the perturbation series results in a temperature-independent error in the entropy.

### IV. LIQUID COPPER

The case of liquid copper, represented by an embedded atom potential [13], with a \( 1/r^{12} \) reference potential, is considered as a realistic example of a dense fluid. The first three cumulants are evaluated by direct Monte Carlo sampling of the canonical distribution of the reference system. The system consists of 256 atoms in a cubic periodic cell. The reference is taken to be 0.14 nm. This is arbitrary, since only the combination \( \epsilon \sigma^{12} \) enters, but it is convenient, and allows \( \epsilon \) to take on reasonable values. The parameter \( \epsilon \) is treated as variational. As described above, the cumulants \( \kappa_n \) for \( n \geq 2 \) are indicative of the convergence of the series, while the first cumulant contains a large contribution from the cohesive energy, analogous to the term \( \phi - \phi_0 \) in the harmonic case. To the extent that \( \kappa_2/T^2 \), \( \kappa_3/T^3 \) are independent of \( T \), this case is similar to the harmonic case, suggesting that convergence is independent of \( T \). Higher order cumulants have increasing statistical errors, so third order was chosen as a practical limit.

Two cases are considered, one with fixed \( \epsilon \), and one with \( \epsilon \) approximately optimized at each temperature. The optimization process was to vary \( \epsilon \) so as to minimize \( \kappa_2 \). Figure 1 illustrates the optimization process for liquid Cu at \( T = 7200 \, \text{K} \) and \( \rho = 0.08467 \, \text{Å}^{-3} \). The free energy of the reference system as parameterized by Young and Rogers [15] was used. At this temperature, the optimum value of \( \epsilon \), in the sense of minimizing \( F_1 \), is approximately 2.5 \( E_h \), where \( E_h \) denotes the Hartree energy, \( E_h = 27.2114 \, \text{eV} \). At this value, \( \kappa_2 \) is also minimized, and \( \kappa_3 \) is small. So, variational optimization corresponds approximately to optimizing the convergence of the series. Subsequently, \( \epsilon \) is optimized by minimizing \( \kappa_2 \).

Figure 2 shows the second and third cumulants as functions of temperature, evaluated with both fixed and optimized \( \epsilon \). The plots show the dimensionless cumulants, \( \kappa_n/T^n \), as appear in the expansion for \( \beta \Delta F \). With fixed parameters, the dimensionless second cumulant varies non-monotonically with \( T \), initially decreasing, then increasing. The dimensionless third cumulant increases in magnitude with \( T \) over the whole range. With optimized \( \epsilon \), the variation of the cumulants is greatly reduced, with \( \kappa_2/T^2 \) increasing slowly with \( T \) and \( \kappa_3/T^3 \) remaining nearly constant. This indicates that the convergence of the series is nearly independent of \( T \). The absolute ratio of the third to second order terms, \( \beta \kappa_3/\beta^2 \kappa_2 \) ranges from 0.01(27) to 0.46(19) from low to high temperature, with fixed \( \epsilon \), and from 0.12(12) to 0.12(16) with optimized \( \epsilon \). At the lowest temperature,
3600 K, the third order contribution to the free energy is \(2.0 \times 10^{-5} \, E_h/\text{atom} \) (0.5 meV/atom), indicating that it is very small in practical terms.

V. AL CRYSTAL

The final example considered here is Al in the fcc crystalline state. The system potential energy surface is defined by \textit{ab initio} DFT energies, and the reference potential is harmonic. The DFT potential energy surface is evaluated using the plane wave code Abinit \cite{16,17} for a 108 atom cell consisting of 3\(^3\) conventional fcc cells. The JTH PAW data \cite{18} was used, and \(E_{\text{cut}}\) was set to 20 \(E_h\). Occupations were determined using the “cold smearing” option (occopt = 4) with the smearing parameter set to 0.010 \(E_h\). The Brillouin zone was sampled with a 2\(^3\) shifted \(k\)-point mesh. The tolerance for SCF convergence was \(10^{-6} E_h\).

The reference potential was harmonic, with force constants defined by an axially symmetric model \cite{19}. Ref. \cite{19} fitted an eighth neighbor model to the phonon dispersion data. In order to test the perturbative expansion, the force constants were truncated at second neighbors. The perturbation series then has to account for deficiencies in the short-range model, as well as anharmonic effects. The reference free energy is \(F_0 = 3NT \ln (\hbar \omega_0 / T) - 1/3\), where \(\omega_0 = \exp \left( \frac{\ln \omega}{BZ} + 1/3 \right)\) is the logarithmic moment of the phonon frequencies and \(\langle BZ \rangle\) denotes an average over wave vectors and polarizations in the Brillouin zone. This average is evaluated on an 8\(^3\) shifted \(k\)-point grid, which gives convergence to 1 part in \(10^4\).

Nuclear coordinates were sampled from the canonical distribution of the reference harmonic model using standard Metropolis Monte Carlo \cite{21}. The configurations were equilibrated over 2000 sweeps consisting of one attempted move of each atom. Then, configurations were sampled every 500 sweeps for evaluation of their DFT energy. In the present case, 100 samples were generated for each thermodynamic state. These configurations were distributed to separate directories for DFT energy calculations. The results were gathered afterward, and the terms in the perturbation series were evaluated as ensemble averages over the sample. Statistical errors were estimated by breaking up the sample into four sub-samples. Reported error bars are one standard deviation. This example is meant to be representative of what would be feasible for a broad scan of thermodynamic states using an \textit{ab initio} potential energy surface.

The resulting Helmholtz free energies for Al at the fixed lattice parameter \(a \approx 7.646 a_0\) (4.046 Å) are shown in figure \ref{fig:Al_free_energy}. The second order contribution to the free energy increases in magnitude from 0.4 – 2.8 \times 10^{-4} \(E_h/\text{atom}\) (1.7-6 meV/atom) over the temperature range from 300 to 900 K. The third order correction to the free is generally small, around 0.1 \(E_h/\text{atom}\) (3 meV/atom) or less, and comparable to its statistical uncertainty. At 300 K, the ratio of the third order to the second order term is 0.13 (39), while at 900 K the ratio is 0.04 (28) indicating good convergence. At the 900 K, statistical errors in the second order free energy are 1.6 \times 10^{-5} \(E_h/\text{atom}\) (0.4 meV/atom). All indications are that the truncation error of the perturbation series and the statistical errors are small, on the order of a few meV/atom.

VI. CONCLUSIONS

The perturbation series introduced by Zwanzig \cite{6} has properties which are advantageous for the efficient evaluation of bulk free energies from \textit{ab initio} potential energy surfaces. However, the presence of increasing powers of the inverse temperature suggests that the series might not be expected to converge well for condensed phases. It has been shown here, for the case that both the system and reference potential are harmonic, that the cumulants \(\kappa_n \propto T^n\) for \(n \geq 2\), and thus that the convergence of the series is independent of \(T\). In more realistic examples of liquid Cu and fcc Al, using smooth reference potentials, numerical results indicate that the truncation error at second order is a few meV/atom or less.

There is a trade-off between the accuracy of a high order expansion and the statistical error, which increases for high order cumulants. The results here suggest that a practical procedure is to use the second order approximation, while evaluating the third order term to monitor convergence. In the Al results obtained here, the third order term was within one standard deviation of zero in most cases.

In the case of fcc Al, the statistical errors of the second order free energy were less than 1 meV/atom with only
100 evaluations of the *ab initio* energy. This is notable because to achieve this statistical accuracy in the energy, for example, with *ab initio* molecular dynamics would usually require a much larger number of *ab initio* force and energy evaluations. This efficiency stems from two main sources. Because the ensemble averages being evaluated are over the canonical distribution of the reference system, equilibration and the generation of independent samples is done on the fast reference potential. Because the energy fluctuations of the reference and system potentials are correlated, the fluctuations of the energy difference are much smaller than the fluctuations of the energies themselves. In summary, the cumulant expansion of the free energy, when used with realistic, smooth, reference potentials, affords an efficient method with small errors for low-temperature states such as solids and dense liquids.

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