11.2.4: Thermodynamics from path integrals

Although general functions of momentum are difficult (though not intractable) to evaluate by path integration, certain functions of momentum (and position) can be evaluated straightforwardly. These are thermodynamic quantities such as the energy and pressure, given respectively by

$$E = -\frac{\partial}{\partial\beta}\ln Q(\beta, V)$$

$$P = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q(\beta, V)$$

We shall derive estimators for these two quantities directly from the path integral expression for the partition function. However, let us work with the partition function for an ensemble of 1-particle systems in three dimensions, which is given by

$$Q(\beta, V) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right] \tag{11.2.4.1}$$

Using the above thermodynamic relation, the energy becomes

$$\begin{aligned} E &= -\frac{1}{Q}\frac{\partial Q}{\partial\beta} \\ &= \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right] \\ &\qquad\times\left[\frac{3P}{2\beta}-\sum_{i=1}^{P}\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_i)\right] \\ &= \lim_{P\to\infty}\langle\varepsilon_P(\mathbf{r}_1,\dots,\mathbf{r}_P)\rangle \end{aligned}$$

where

$$\varepsilon_P(\mathbf{r}_1,\dots,\mathbf{r}_P) = \frac{3P}{2\beta}-\sum_{i=1}^{P}\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_i)$$

is the thermodynamic estimator for the total energy. Similarly, an estimator for the internal pressure can be derived using $P = kT\partial\ln Q/\partial V$. As we have done in the past for classical systems, the volume dependence can be made explicitly by introducing the change of variables:

$$\mathbf{r}_k = V^{1/3}\mathbf{s}_k \tag{11.2.4.2}$$

In terms of the scaled variables s_k, the partition function expression reads:

$$Q(\beta, V) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}V^P\int ds_1\cdots ds_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2V^{2/3}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2+\frac{1}{P}U(V^{1/3}\mathbf{s}_i)\right)\right] \tag{11.2.4.3}$$

Evaluating the derivative with respect to volume gives the internal pressure:

$$\begin{aligned} P &= \frac{1}{\beta Q}\frac{\partial Q}{\partial V} \\ &= \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2} V^P \int ds_1\cdots ds_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2 V^{2/3}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2+\frac{1}{P}U(V^{1/3}\mathbf{s}_i)\right)\right] \\ &\qquad \times\left[\frac{P}{\beta V}-\frac{1}{3}m\omega_P^2 V^{-1/3}\sum_{i=1}^{P}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2-\frac{1}{P}\sum_{i=1}^{P}\frac{\partial U}{\partial(V^{1/3}\mathbf{s}_i)}\cdot\frac{1}{3}V^{-2/3}\mathbf{s}_i\right] \\ &= \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right] \\ &\qquad \times\left[\frac{P}{\beta V}-\frac{1}{3V}m\omega_P^2\sum_{i=1}^{P}(\mathbf{r}_{i+1}-\mathbf{r}_i)^2-\frac{1}{3VP}\sum_{i=1}^{P}\frac{\partial U}{\partial\mathbf{r}_i}\cdot\mathbf{s}_i\right] \\ &= \lim_{P\to\infty}\langle p_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)\rangle \end{aligned}$$

where

$$p_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)=\frac{P}{\beta V}-\frac{1}{3V}\sum_{i=1}^{P}\left[m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\mathbf{r}_i\cdot\frac{\partial U}{\partial\mathbf{r}_i}\right] \tag{11.2.4.4}$$

is the thermodynamic estimator for the pressure. Clearly, both the energy and pressure will be functions of the particle momenta, however, because they are related to the partition function by thermodynamic differentiation, estimators can be derived for them that do not require the off-diagonal elements of the density matrix.