On the density of volume states in the isobaric ensemble

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The Gibbs or information entropy, \( S = -k_B \sum_i \varphi_i \ln \varphi_i \), in the continuum limit becomes\(^1\)

\[
S = -k_B \int dx \, \nu(x) \varphi(x) \ln \varphi(x),
\]

where \( \nu(x) \) is the density of states, \( \varphi(x) \) is the probability of a particular state, and \( \omega(x) = \varphi(x) \nu(x) \) is the probability density. \([i.e., \omega(x) \, dx \text{ is the probability of finding the system between } x \text{ and } x + dx]\). The density of states is essential for the entropy to be invariant under coordinate transformations, \([i.e., \text{for } y = y(x), \nu_i(y) \, dy = \nu_i(x) \, dx]\). Given some average quantity \( \langle f(x) \rangle \), the maximum entropy principle yields the probability density\(^1\)

\[
\omega(x) = Z^{-1} e^{-\lambda f(x)} \nu(x),
\]

where the partition function is

\[
Z = \int e^{-\lambda f(x)} \nu(x) \, dx.
\]

Again the partition function is formally invariant under coordinate transformations.

It is straightforward to transform the density of states between different representations, and if the continuum is obtained by a limiting process from the discrete case, one has an explicit expression for it. More generally, when the continuum is simply postulated, in the language of Bayesian statistics \( \nu(x) \) represents the \emph{a priori} probability density, the initial distribution to be used in the absence of any information. \([This may be seen from the above, where if \langle f(x) \rangle \text{ is not given then } \lambda = 0 \text{ and } \omega(x) \propto \nu(x).]\) Jeffreys\(^2\) suggested the appropriate form in two cases, and these were rederived by Jaynes\(^1\) using group theoretic techniques.\(^3\) If \( x \) is a location parameter, then \( \nu(x) \) is a constant. An example of a location parameter in classical statistical mechanics is the coordinates of a particle in real and momentum space, and conventionally the value of the constant is chosen to be the cube of Planck’s constant. The second case is if \( x \) is a scale parameter, then \( \nu(x) \propto x^{-1} \). In the absence of any other information the volume simply sets the size of a system, and the point of this note is that

\[
\text{the volume should be regarded as a scale parameter with density of states } V^{-1}.
\]

In general the density of states is slowly varying, and if the probability distribution is sharply peaked, as it is in the thermodynamic limit, then one can replace \( \nu(x) \) by \( \nu(x) \), a constant, which can be neglected. Therefore, apart from academic interest, the practical import of the result given above is limited to finite-sized systems and to systems with large fluctuations. Specifically, it would appear to be essential to apply the result to simulations in the isobaric ensemble that may be restricted to small system size by computational limits, or by particular application (such as to pores, bubbles, or clusters). If an accurate equation of state is required, then the density of volume states should also be included in the simulation, and it would appear to be pointless to attempt other finite-size corrections if the configurations themselves have been generated with an incorrect weight. The density of volume states also appears necessary in simulations of the critical point, of the line of spinodal decomposition, and of liquid–gas coexistence.

In view of this interpretation of the volume as a scale parameter, the partition function for a fluctuating volume ensemble is

\[
Z(N,p,T) = N \int e^{-\beta p V - \beta F(N,V,T)} V^{-1} \, dV,
\]

where \( \beta = 1/k_B T \) is the inverse temperature, \( p \) is the pressure, and \( F(N,V,T) \) is the Helmholtz free energy and where the proportionality constant for the density of states has been set equal to \( N \), for reasons that will become clear below. This expression yields a dimensionless partition function, whereas the orthodox formulation requires an \emph{ad hoc} constant with the dimensions of inverse length cubed; Sack\(^4\) advocated \( \beta p \), but with this choice the pressure derivative of the free energy yields the average volume only to order \( N^{-1} \). Note that usually simulations use the cube length \( L \) as the unit of length. The present expression is invariant under this transformation, \( dV/V = 3dL/L \), whereas when the density of states is neglected, the equation has a different form in the new coordinate system, \( dV = 3L^2 dL \). In contrast to the present expression, conventional statistical mechanics texts, \([e.g., \text{Eq. (2.3.25) of Ref. 5}], \) and computer simulation guides, \([e.g., \text{Eq. (2.28) of Ref. 6}], \) neglect the density of volume states \( \nu(V) = N/V \). A random sampling of the literature has not revealed a single isobaric simulation that includes the density of volume states. Regrettably, the author’s own morphobaric simulations suffer in this regard.\(^7-9\)

It is easy to demonstrate that this is the correct expression. For an ideal gas \( \exp(-\beta \frac{V}{T} V^N N!) \), and

\[
Z^d = N \int_0^{\infty} e^{-\beta p V} \left( \frac{V^N}{N^{N!}} V^{-1} \right) \, dV = (\beta p)^{-N}.
\]

Hence \( -\partial \ln Z^d/\partial \beta = \langle V \rangle = N/\beta p \), or \( p = N k_B T \langle V \rangle \). This is evidently the correct expression, whereas if one neglects the density of states one obtains \( p = (N+1) k_B T \langle V \rangle \), which is wrong. As stated above, the error is only important for finite-sized systems.

Choosing the proportionality constant for the density of states such that \( \nu(V) = N/V \) means that for the ideal gas the Gibbs free energy, \( G = -k_B T \ln Z \) satisfies the usual
relations. Further, the entropy of the isobaric isothermal ensemble consists of the uncertainty in the volume of the system, Eq. (1), plus the uncertainty in the internal state of the fluid,

$$ S = -k_B \int_0^\infty \omega(V) \ln \frac{\omega(V)}{\nu(V)} dV + \int_0^\infty \omega(V)S(N,V,T) dV. \quad (7) $$

For the ideal gas, using the entropy of the canonical ensemble $S(N,V,T) = 3Nk_B/2 - k_B \ln \Lambda^3 V^{-N}/N!$, one obtains

$$ S = 5Nk_B/2 - Nk_B \ln N \Lambda^3/(V), \quad (8) $$

which equals that of the canonical ensemble in the thermodynamic limit (otherwise it is presumably strictly greater than the latter), and which satisfies the usual relation, $S = -\partial G / \partial T$. Hence this choice of the proportionality constant fixes the arbitrary zero for the free energy so that the standard results for the ideal gas are obtained.

An exact solution also exists for one-dimensional hard rods (Tonks gas). For $N$ rods of length $d$ whose centers are confined to a line of length $L$, the canonical partition function is $Z(N,L,T) = \Lambda^{-N} \left[ L - (N - 1)d \right]^{N}/N!$, which yields Rayleigh’s equation of state, $p = Nk_B T / [L - (N - 1)d]$. Noting that the length of the line must be greater than the close packed volume $(N - 1)d$, the isobaric partition function is

$$ Z(N,p,T) = \Lambda^{-N} \int_{(N - 1)d}^\infty \frac{N\Lambda(N,L,T) e^{-\beta p L}}{L - (N - 1)d} dL \quad \text{ where } \quad p = k_B T / (N - 1)d. $$

Divergence with respect to pressure yields the average length and an equation of state identical to the canonical result. This example suggests that in general the lower limit on the volume integral should be taken as the close packed volume, and that the consistent density of states should be used.\(^3\)

Beyond the ideal gas, if fluctuations are small it is permissible to use a Taylor expansion of the density of states about the average volume, $V^{-1} = \langle V \rangle^{-1} [1 - (V - \langle V \rangle)/(V) + O((V - \langle V \rangle)^2)] = \langle V \rangle^{-1} e^{-1/V(x)} + O(V - \langle V \rangle)^2$. Hence,

$$ Z(N,p,T) \approx N e^{p' T / \langle V \rangle} \int_0^\infty e^{-\beta p' V} e^{-\beta F(N,V,T)} dV, $$

where $p' = p + k_B T / \langle V \rangle$.\(^10\)

One sees that for systems with small fluctuations, neglecting the density of states is equivalent to using an effective pressure that is greater than the actual pressure by an amount $k_B T / \langle V \rangle$. This error is non-negligible for small systems, and for low-pressure systems, such as a (deeply) subcritical metastable liquid near coexistence.

The effect of large fluctuations can be demonstrated using a formal expression for the error in the average volume that involves the isothermal compressibility. If one denotes quantities calculated without the density of volume states by a prime, then since the exact average volume can be written as the ratio of partition functions, $\langle V \rangle = Z'/Z$, it is easy to show that the erroneous average volume is given by

$$ \langle V \rangle' = \langle V \rangle + \frac{\langle (V - \langle V \rangle)^2 \rangle}{\langle V \rangle}. $$

This formally exact expression shows that in general the density calculated without the density of volume states is smaller than the actual density (for a given pressure). It may be possible to use this expression to approximately correct those existing results, or at least to estimate the error. The correction is of order unity for systems away from critical points and lines of spinodal decomposition. However, near these regions the correction is of the same order as the volume itself, which suggests that existing isobaric simulation results for these regions should be treated with caution. Insofar as the coexistence line lies near the line of spinodal decomposition (the two lines coincide in the critical region), the error can also be large for simulations of liquid–gas and other coexistence. One notes that the Gibbs ensemble technique has been developed to explore coexistence via coupled volume and particle number fluctuations. From the present analysis for the density of volume states, the partition function for the Gibbs ensemble of two coupled but noninteracting systems is $Z = \sum_{N_1=0}^{N} N_1(N_1 - 1) \int_w^V e^{-\beta F(N_1,V_1,T)} dV_1 / (V_1 - W)(V_1 - V_1).$\(^11\)

[Note that there is no contribution when either box is empty. Note also that the (immaterial) preconstant has been chosen to reproduce the ideal gas Helmholtz free energy, and that one could multiply this by $V^{1/3} / \Lambda_0$ to include a contribution from the motion of the wall. Note finally that the lower limit on the integration is the $N_1$-dependent close packed volume.] This differs from the usual expression by the density of states,\(^3\) which will affect both volume and particle interchanges.

In summary, the correct density of volume states will make a measurable difference in isobaric simulations of small systems, of accurate equations of state, and of the critical, spinodal, and possibly coexistence regions. However, even when it has no greater influence than other finite-size effects, which is probably the case in the majority of isobaric simulations, there appears to be no reason not to include the exact density of volume states given here.


\(^{12}\) If $x \in [a,b]$, then $\pi(x) = 1/(x-a)(b-x)$, which yields the location and scale parameters as limiting cases.


