

COMMENTS

Comment on “Length Scale for the Constant Pressure Ensemble: Application to Small Systems and Relation to Einstein Fluctuation Theory”

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In an article published in this journal early last year, Koper and Reiss¹ introduced a volume scale that allows the partition function within the isothermal–isobaric ensemble (pressure, temperature, and particle number are held fixed) to be represented by a dimensionless integral. The need to introduce a volume or length scale arises because the relevant partition function involves a sum over a set of unspecified system volumes. Replacing the sum by an integral to include *all volumes* results in a partition function that is not dimensionless but has the dimensions of volume. In the thermodynamic limit, the sum over discrete unspecified volumes yields a completely negligible error,² in essence because only the maximum term in the sum was important. However, as emphasis has turned to the theory of small systems (e.g., clusters³ and microemulsions⁴), there is an obvious need to include all the terms and obtain the correct partition function as an integral over volume.

For a system composed of N particles, maintained at a temperature T , and subject to a constant external pressure p , Koper and Reiss showed that the partition function Δ , if evaluated over a continuous set of system volumes, is

$$\Delta = \int_V \frac{p''}{kT} Q(N, V, T) e^{-pV/kT} dV \quad (1)$$

where

$$\frac{p''}{kT} = \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T} \quad (2)$$

provides the appropriate length scale of inverse volume such that Δ is dimensionless. Note that p'' is the pressure of the system at volume V . (Koper and Reiss correctly state that the meaning of p'' in eq 2 is not necessarily that of a *pressure* since for a small system there are usually additional independent thermodynamic variables (e.g., surface area, curvature, etc.) that need to be considered. However, it is convenient to refer to p'' as a pressure even though it denotes a specific volume derivative of Q .) In the above equations, $Q(N, V, T)$ is the canonical ensemble partition function for a system containing N particles in a volume V at the given temperature T , while k is Boltzmann's constant. Equation 1 was derived by eliminating all redundant microstates that had the same volume. Koper and Reiss found that (eq 4.20 in their paper)

$$G = -kT \ln T - kT \ln \Delta \quad (3)$$

where G is the Gibbs energy and $kT \ln T$ is negligible in the

thermodynamic limit. However, this result is inconsistent with their eq 4.9 in which

$$\Omega_t = \Delta \exp \left[\frac{\bar{U} + p\bar{V} + T S_0(\bar{U}_0, \bar{V}_0, N_0)}{kT} \right] \quad (4)$$

Ω_t is the total hypervolume available to an isolated system composed of N_t particles at a fixed volume V_t and energy U_t . The system is divided into two parts: the subsystem of interest (not necessarily macroscopic) and a bath of macroscopic size. The external bath imposes a constant temperature T and pressure p on the subsystem. The subsystem is described by U , V , and N while the bath is described by U_0 , V_0 and N_0 . An overbar above a variable denotes the average (equilibrium) value. If we take the logarithm of both sides of eq 4, we find that

$$\ln \Omega_t = \frac{S_t}{k} = \ln \Delta + \frac{\bar{U}}{kT} + \frac{p\bar{V}}{kT} + \frac{S_0}{k} = \ln \Delta + \frac{\hat{H}}{kT} + \frac{S_0}{k} \quad (5)$$

where we define⁵

$$\hat{H} \equiv \bar{U} + p\bar{V} \quad (6)$$

Since the entropy is additive, we note that the total entropy of the isolated system must be equal to the sum of the individual entropies of the bath and subsystem ($S_t = S + S_0$). Therefore, if we let

$$\hat{G} \equiv \bar{U} + p\bar{V} - TS = \hat{H} - TS \quad (7)$$

we find that⁵

$$\hat{G} = -kT \ln \Delta(N, p, T) \quad (8)$$

Note that \hat{G} is not equivalent to the Gibbs energy of the subsystem, as Koper and Reiss suggest in eq 3, but can be thought of as a modified Gibbs energy due to the appearance of p (and not the internal pressure) in eq 7. Koper and Reiss obtained eq 3 by ignoring the temperature dependence of p'' in their eq 4.13.⁶ Equation 8 is applicable to a system of any size and is consistent with previous formulations² for systems in the thermodynamic limit. Koper and Reiss showed that $p'' = p$ for a macroscopic system (eq 6.5 in their paper) and, in this limit only, does \hat{G} necessarily equal the Gibbs energy G of the subsystem.

We can now determine what thermodynamic variables are related to the derivatives of \hat{G} . For a system in which a constant external pressure p is imposed, we note that the differential change in the internal energy \bar{U} is equal to⁵

$$d\bar{U} = T dS - p d\bar{V} + \mu dN \quad (9)$$

where $-p d\bar{V}$ is the work performed by the system against the fixed external pressure p and μ is the chemical potential. Using eqs 7 and 9, one can show that

$$\left(\frac{\partial \hat{G}}{\partial T} \right)_{p, N} = -S \quad (10)$$

$$\left(\frac{\partial \hat{G}}{\partial p}\right)_{T,N} = \bar{V} \quad (11)$$

$$\left(\frac{\partial \hat{G}}{\partial N}\right)_{T,p} = \mu \quad (12)$$

The above relations are identical to earlier results obtained for both small⁵ and macroscopic² systems.

The effect of using the required volume scale can be demonstrated by analyzing a system composed of ideal gas particles. In three dimensions, the canonical ensemble partition function is given by⁷

$$Q(N,V,T) = V^N/N!\Lambda^{3N} \quad (13)$$

Noting that $p''/kT = N/V$ (eq 2) we find upon using eq 1 that

$$\Delta = (kT/p\Lambda^3)^N \quad (14)$$

and therefore

$$\hat{G} = NkT \ln(p\Lambda^3/kT) \quad (15)$$

From eq 11 we find that $\bar{V} = NkT/p$. If one neglects to use the volume scale in eq 1, then one obtains $\Delta = (kT/p\Lambda^3)^{N+1}$ and $\bar{V} = (N+1)kT/p$, a difference that is significant when dealing with a finite system.

We can determine the average pressure, \bar{p}'' , of the ideal gas from

$$\bar{p}'' = \Delta^{-1} \int_0^\infty p''(p''/kT)Q(N,V,T)e^{-pV/kT} dV \quad (16)$$

One finds that

$$\bar{p}'' = \frac{p}{1 - 1/N} \quad (17)$$

showing that an ideal gas exhibits system size effects. The above equation was obtained by Koper and Reiss (eq 6.6 in their paper), by extending, in approximation, the maximum term method to a system not of macroscopic size. However, the approximation proved to be adequate in that eq 17 is exact and is valid for all system sizes. As expected, $\bar{p}'' = p$ in the thermodynamic limit ($N \rightarrow \infty$). We also find that eq 15 yields the following result

$$\mu = kT \ln \frac{p\Lambda^3}{kT} = \frac{\hat{G}}{N} \quad (18)$$

Nevertheless, the equivalence of μ and \hat{G}/N should not be expected to hold, in general, for small systems.

The effect of system size can be further demonstrated if we obtain Δ for the one-dimensional hard rod fluid. If we have N hard rods of diameter σ within a length (volume) L , the canonical ensemble partition function is⁸

$$Q(N,L,T) = \frac{[L - (N-1)\sigma]^N}{\Lambda^N N!} \quad (19)$$

One can therefore show that

$$\hat{G} = -kT \ln \Delta(N,p,T) = p(N-1)\sigma + NkT \ln(p\Lambda/kT) \quad (20)$$

and

$$\bar{p}'' = \frac{p}{1 - 1/N} \quad (21)$$

We also notice from eq 20 that

$$\left(\frac{\partial \hat{G}}{\partial N}\right)_{T,p} - \frac{\hat{G}}{N} = \mu - \frac{\hat{G}}{N} = \frac{p\sigma}{N} \quad (22)$$

where we have assumed that the discrete variable N is large enough to justify its use as a differential. This difference, of course, becomes negligible in the thermodynamic limit.

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References and Notes

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