Density and energy fluctuations in the grand canonical ensemble: correspondence with other ensembles

In a grand canonical ensemble, the variables N and E, for any member of the ensemble, can lie anywhere between zero and infinity. Therefore, on the face of it, the grand canonical ensemble appears to be very different from its predecessors−the canonical and the microcanonical ensembles. However, as far as thermodynamics is concerned, the results obtained from this ensemble turn out to be identical with the ones obtained from the other two. Thus, in spite of strong facial differences, the overall behavior of a given physical system is practically the same whether it belongs to one kind of ensemble or another. The basic reason for this is that the "relative fluctuations" in the values of the quantities that vary from member to member in an ensemble are practically negligible. Therefore, in spite of the different surroundings which different ensembles provide to a given physical system, the overall behavior of the system is not significantly affected.

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \alpha} q(z,V,T) = z\frac{\partial}{\partial z} q(z,V,T)_{V,T}$$

$$\frac{\partial \bar{N}}{\partial \alpha} = -\frac{\sum_{r,s} N_r^2 \exp\{-\alpha N_r - \beta E_s\}}{\sum_{r,s} \exp\{-\alpha N_r - \beta E_s\}} + \frac{\left[\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)\right]^2}{\left[\sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right]^2}$$

$$\left.\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta, E_S} = -\left\langle N^2 \right\rangle + \left\langle N \right\rangle^2 = -\left\langle (\Delta N)^2 \right\rangle$$

$$(\Delta N)^2 = -\left.\frac{\partial \bar{N}}{\partial \alpha}\right)_{T,V} = kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)$$

$$e^{-\alpha} = e^{\frac{\mu}{KT}} = z \qquad \frac{\partial z}{\partial \alpha} = -e^{-\alpha} = -z$$

$$\frac{\partial}{\partial \alpha} = \frac{\partial z}{\partial \alpha}\frac{\partial}{\partial z} = -z\frac{\partial}{\partial z} = kT\frac{\partial}{\partial \mu}$$

$$e^{-\alpha} = e^{\frac{\mu}{KT}} = z$$

$$\frac{\partial z}{\partial \mu} = \frac{1}{KT} e^{\frac{\mu}{KT}} = \frac{1}{KT} z$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial \mu}\frac{\partial \mu}{\partial z} = \frac{kT}{z}\frac{\partial}{\partial \mu}$$

$$(\Delta N)^2 = -\left.\frac{\partial \bar{N}}{\partial \alpha}\right)_{T,V} = kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)$$

$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} = \frac{kT}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = \frac{KTv^2}{V^2}\left(\frac{\partial \left(V/v\right)}{\partial \mu}\right)_{T,V} = -\frac{KT}{V}\left(\frac{\partial v}{\partial \mu}\right)_T \qquad ; v = \frac{V}{\bar{N}}$$

$$= \frac{-kT}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{kT}{V}\kappa_T = \frac{kT}{V}\frac{1}{B}$$

$$E = TS - PV + \mu N$$

$$dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

$$dE = TdS - PdV + \mu dN$$

$$SdT - VdP + Nd\mu = 0$$

$$VdP = Nd\mu \qquad \frac{V}{N} dP = d\mu \qquad vdP = d\mu$$

Thus, the relative root-mean-square fluctuation in the particle density of the given system is *ordinarily* $O(N^{-1/2})$ and, hence, negligible. However, there are exceptions, like the ones met with in situations accompanying *phase transitions*. In those situations, the compressibility of a given system can become excessively large, as is evidenced by an almost "flattening" of the isotherms. Under these circumstances, the derivative $(\partial v/\partial P)_T$, and hence the quantity κ_T, can very well be $O(N)$; the relative root-mean-square fluctuation in the particle density n can then be $O(1)$. Thus, in the region of phase transitions, especially at the critical points, we expect to encounter unusually large fluctuations in the particle density of the system. Such fluctuations indeed exist and account for phenomena like *critical opalescence*. It is clear that under these circumstances the formalism of the grand canonical ensemble could, in principle, lead to results which are not necessarily identical with the ones following from the corresponding canonical ensemble. In such cases, it is the formalism of the grand canonical ensemble which will have to be preferred because only this one will provide a correct picture of the actual physical situation.

American Journal of Physics, Vol. 67, No. 12, pp. 1149–1151, December 1999

Up: Issue Table of Contents
Go to: Previous Article | Next Article
Other formats: HTML (smaller files) | PDF (39 kB)

Fluctuations in the number of particles of the ideal gas: A simple example of explicit finite-size effects

F. L. Román, A. González, J. A. White, and S. Velasco

Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Salamanca, 37008 Salamanca, Spain

Received: 29 October 1998; accepted: 10 May 1999

The fluctuations in the number of particles of the ideal gas are calculated using the canonical and the grand canonical ensembles. The two results differ by a factor which accounts for the relative size of the total volume and the subvolume where the canonical ensemble fluctuations are calculated. This factor gives a simple example of explicit finite-size effects, because it arises from considering a fixed number of particles in the canonical ensemble. Our simulation results for the isothermal compressibility of the hard disk fluid with a finite number of particles are improved by applying this correction. © *1999 American Association of Physics Teachers.* [S0002-9505(99)00712-6]

$$U \equiv \left\langle E \right\rangle = \frac{\sum_{r,s} E_s e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = -\frac{\partial q}{\partial \beta} = kT^2\frac{\partial q}{\partial T}$$

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_{r,s} E_s^2 e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} + \frac{\left[\sum_{r,s} E_s e^{-\beta E_s - \alpha N_r}\right]^2}{\left[\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right]^2} = -\left\langle E^2 \right\rangle + \left\langle E \right\rangle^2 = -\left\langle (\Delta E)^2 \right\rangle$$

$$\left\langle (\Delta E)^2 \right\rangle \equiv \left\langle E^2 \right\rangle - \left\langle E \right\rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right) = -\left(\frac{\partial U}{\partial T}\frac{\partial T}{\partial \beta}\right) = kT^2\left(\frac{\partial U}{\partial T}\right)$$

Grand Canonical Ensemble (T, V, μ)

$$\left\langle (\Delta E)^2 \right\rangle \equiv kT^2\left(\frac{\partial U}{\partial T}\right)_{V,z}$$

$$\left.\frac{\partial X}{\partial Y}\right)_Z = \left.\frac{\partial X}{\partial Y}\right)_W + \left.\frac{\partial X}{\partial W}\right)_Y \left.\frac{\partial W}{\partial Y}\right)_Z$$

$$\left.\frac{\partial U}{\partial T}\right)_{V,z} = \left.\frac{\partial U}{\partial T}\right)_{V,N} + \left.\frac{\partial U}{\partial N}\right)_{V,T} \left.\frac{\partial N}{\partial T}\right)_{V,z}$$

$$\left.\frac{\partial U}{\partial T}\right)_{V,z} = C_V + \left.\frac{\partial U}{\partial N}\right)_{V,T} \left.\frac{\partial N}{\partial T}\right)_{V,z}$$

$$\left.\frac{\partial U}{\partial N}\right)_{V,T} = ? \qquad \left.\frac{\partial N}{\partial T}\right)_{V,z} = ?$$

$$\left.\frac{\partial U}{\partial N}\right)_{V,T} = \mu + T\left(\frac{\partial S}{\partial N}\right)_{T,V}$$

Since: $dU = TdS - PdV + \mu dN$

$$\left(\frac{\partial S}{\partial N}\right)_{T,V} = ?$$

The answer is: $\left(\frac{\partial S}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial T}\right)_{N,V}$ But why?

dA = $\cancel{\text{d}}$E - T$\cancel{\text{d}}$S - SdT $\oplus$

$\cancel{\text{d}}$E = T$\cancel{\text{d}}$S – PdV + µdN

dA = -SdT - PdV + µdN

dE = TdS – PdV + µdN	dA = -SdT - PdV + µdN
(S, V, N)	(T, V, N)

$$dA = -SdT - PdV + \mu dN$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -S \quad \& \quad \left(\frac{\partial A}{\partial N}\right)_{V,T} = \mu$$

$$\frac{\partial}{\partial N}\left[\left(\frac{\partial A}{\partial T}\right)_{V,N}\right]_{V,T} = \frac{\partial}{\partial T}\left[\left(\frac{\partial A}{\partial N}\right)_{V,T}\right]_{V,N}$$

$$-\left[\frac{\partial S}{\partial N}\right]_{V,T} = \left[\frac{\partial \mu}{\partial T}\right]_{V,N}$$

$$\left.\frac{\partial U}{\partial N}\right)_{V,T} = \mu + T\left(\frac{\partial S}{\partial N}\right)_{T,V}$$

$$\boxed{\left.\frac{\partial U}{\partial N}\right)_{V,T} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}}$$

Let's go through the second question which was:

$$\left.\frac{\partial N}{\partial T}\right)_{V,z} = ?$$

$$\left.\frac{\partial N}{\partial T}\right)_{V,z} = ?$$

$$\left.\frac{\partial X}{\partial Y}\right)_Z = \left.\frac{\partial X}{\partial Y}\right)_W + \left.\frac{\partial X}{\partial W}\right)_Y \left.\frac{\partial W}{\partial Y}\right)_Z$$

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = \left.\frac{\partial N}{\partial T}\right)_{\mu,V} + \left.\frac{\partial N}{\partial \mu}\right)_{T,V} \left.\frac{\partial \mu}{\partial T}\right)_{z,V}$$

$$e^{-\alpha} = e^{\frac{\mu}{kT}} = z \qquad \frac{\mu}{kT} = \ln z \qquad \mu = kT\ln z \qquad \left.\frac{\partial \mu}{\partial T}\right)_{z,V} = \frac{\mu}{T}$$

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = \left.\frac{\partial N}{\partial T}\right)_{\mu,V} + \left.\frac{\partial N}{\partial \mu}\right)_{T,V} \frac{\mu}{T}$$

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = -\left.\frac{\partial N}{\partial \mu}\right)_{T,V} \left.\frac{\partial \mu}{\partial T}\right)_{N,V} + \left.\frac{\partial N}{\partial \mu}\right)_{T,V} \frac{\mu}{T}$$

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = -\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left.\frac{\partial \mu}{\partial T}\right)_{N,V} + \left.\frac{\partial N}{\partial \mu}\right)_{T,V}\frac{\mu}{T}$$

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left(\mu - T\left.\frac{\partial \mu}{\partial T}\right)_{N,V}\right)$$

We previously established that:

$$\left.\frac{\partial U}{\partial N}\right)_{V,T} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}$$

Whence

$$\left.\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left.\frac{\partial U}{\partial N}\right)_{T,V}$$

Which is the answer of our second question

Now we arrive to the point that can finalize the dissuasion on fluctuation
Let's put together all we have found up to now:

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2\left(\frac{\partial U}{\partial T}\right)_{V,z} \qquad \left.\frac{\partial U}{\partial T}\right)_{V,z} = C_V + \left.\frac{\partial U}{\partial N}\right)_{V,T}\left.\frac{\partial N}{\partial T}\right)_{V,z}$$

$$\left.\frac{\partial U}{\partial N}\right)_{V,T} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V} \qquad \left.\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left.\frac{\partial U}{\partial N}\right)_{T,V}$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2\left\{C_V + \left.\frac{\partial U}{\partial N}\right)_{T,V}\left[\frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]\right\}$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2\left\{C_V + \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\right\}$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2\left\{C_V + \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\right\}$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2C_V + kT\left.\frac{\partial N}{\partial \mu}\right)_{T,V}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2$$

$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} = \frac{kT}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} \Rightarrow kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = \overline{(\Delta N)^2}$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2C_V + \overline{(\Delta N)^2}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2$$

$$\left\langle(\Delta E)^2\right\rangle \equiv kT^2C_V + \overline{(\Delta N)^2}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2$$

$$\left\langle(\Delta E)^2\right\rangle_{GrandCan.} \equiv \left\langle(\Delta E)^2\right\rangle_{Can.} + \overline{(\Delta N)^2}\left[\left.\frac{\partial U}{\partial N}\right)_{T,V}\right]^2$$

Formula (14) is highly instructive; it tells us that the mean-square fluctuation in the energy E of a system in the grand canonical ensemble is equal to the value it would have in the canonical ensemble *plus* a contribution arising from the fact that now the particle number N is also fluctuating. Again, under ordinary circumstances, the relative root-mean-square fluctuation in the energy density of the system would be practically negligible. However, in the region of phase transitions, unusually large fluctuations in the values of this variable can arise by virtue of the second term in the formula.