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An approach to the calculation of ensemble fluctuations

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Abstract. An approach is developed for the calculation of fluctuations in an ensemble of systems obeying Maxwell–Boltzmann, Fermi–Dirac or Bose–Einstein statistics, and in which a specified set of physical quantities is conserved. The technique is applied to two situations of interest: in the first only energy is conserved while in the second both energy and number are conserved.

1. Introduction

Consider a set of N identical systems with given total energy E distributed among a set of energy levels $E_1, E_2, \ldots$ and let $g_p (p = 1, 2, \ldots)$ be the number of available states for energy level E_p. We suppose that there are n_p systems in energy level E_p, and the corresponding number of ways of realizing this distribution is then given by the standard expressions

$$W^{\mathrm{M}} = \prod_p \left(\frac{g_p^{n_p}}{n_p!} \right) \qquad W^F = \prod_p \frac{g_p!}{n_p!(g_p - n_p)!} \qquad W^{\mathrm{B}} = \prod_p \frac{(n_p + g_p - 1)!}{n_p!(g_p - 1)!} \tag{1}$$

for Maxwell–Boltzmann, Fermi–Dirac and Bose–Einstein statistics respectively [1]. A basic problem in statistical mechanics is then the calculation of fluctuations of the occupation numbers n_p about their mean distributions in the limit of $n_p \gg 1$. This in general involves a computation of the expectation value of n_p^2 subject to the conservation constraints that

$$\sum_p n_p = N \qquad \text{and} \qquad \sum_p n_p E_p = E \tag{2}$$

are maintained constant, and the standard approach to this has been through the use of the Darwin–Fowler method [1]. The basic point of the present communication is to develop an alternative technique for the calculation of these fluctuations. Our approach is more direct than that of Darwin and Fowler and avoids the use of complex variable theory inherent in their method. It is also readily applied to situations where the number of conservation constraints is less or more than the two given above in (2): for example, the case of photons or phonons in which the number of systems can vary and only the total energy E is constant, or on the other hand, situations in which the conservation constraints (2) are supplemented by conservation of one or more components of the total linear or angular momentum of the systems.

2. Basic formulation of technique

We begin by considering the form of W close to its maximum value. We let $n_p = \nu_p + \gamma_p$ where ν_p are the standard equilibrium distributions (Maxwell–Boltzmann, Fermi–Dirac or Bose–Einstein) which maximize the corresponding W, and then readily obtain

$$W(n_p) = W(\nu_p)\exp\left[-\frac{1}{2}\sum_p\left(\frac{\gamma_p}{\sigma_p}\right)^2\right] \tag{3a}$$

for $|\gamma_p| \ll \nu_p$. Here

$$(\sigma_p^{\mathrm{M}})^2 = \nu_p^{\mathrm{M}} \qquad (\sigma_p^{\mathrm{F}})^2 = \nu_p^{\mathrm{F}}[1-(\nu_p^{\mathrm{F}}/g_p)] \qquad (\sigma_p^{\mathrm{B}})^2 = \nu_p^{\mathrm{B}}[1+(\nu_p^{\mathrm{B}}/g_p)]. \tag{3b}$$

To describe the fluctuations in the occupation numbers we now require to calculate the variance of n_p and the covariance of n_p and n_q when the probability of obtaining the value n_p is given by the distribution (3), and when the possible values of n_p are related by the conservation constraints (2). We have

$$\mathrm{Cov}(n_p, n_q) = \mathrm{Cov}(\gamma_p, \gamma_q) = \sigma_p\sigma_q\mathrm{Cov}(\Delta_p, \Delta_q) \tag{4a}$$

$$\mathrm{Var}(n_p) = \mathrm{Var}(\gamma_p) = \sigma_p^2\mathrm{Var}(\Delta_p) \tag{4b}$$

where $\Delta_p = \gamma_p/\sigma_p$, and it follows from equation (3a) that the probability of obtaining the value Δ_p is proportional to

$$J = \exp\left(-\frac{1}{2}\sum_p \Delta_p^2\right). \tag{5}$$

Now, as mentioned earlier we are interested in situations where there are an arbitrary number of conservation constraints imposed on n_p, and we therefore postulate the existence of M such constraints of the form

$$\sum_p \alpha_{sp} n_p = K_s \qquad (1 \leqslant s \leqslant M) \tag{6a}$$

where the K_s are a set of given constants (equations (2) correspond to $M = 2$ with $\alpha_{1p} = 1$, $\alpha_{2p} = E_p$, $K_1 = N$, $K_2 = E$). Correspondingly there will exist M constraints on the Δ of the form

$$\sum_p a_{sp}\Delta_p = 0 (1 \leqslant s \leqslant M) \tag{6b}$$

where $a_{sp} = \sigma_p\alpha_{sp}$. This means that in equation (5) the number of independent Δ will be M less than the total number of Δ. We can now use the M equations (6b) to express M 'dependent' Δ in terms of the remaining 'independent' ones, leading to the result

$$\Delta^{(s)} = {\sum_q}' \rho_q^{(s)}\Delta_q \qquad (1 \leqslant s \leqslant M) \tag{7}$$

where $\Delta^{(s)} (1 \leqslant s \leqslant M)$ are the 'dependent' Δ, $\sum_q'$ implies a summation over the remaining independent Δ and the coefficients $\rho_q^{(s)}$ can be readily expressed in terms of the a_{sp}. It then follows from equation (5) that

$$J = \exp\left(-\frac{1}{2}{\sum_{p,q}}' T_{pq}\Delta_p\Delta_q\right) \tag{8a}$$

where

$$T_{pq} = \delta_{pq} + \sum_{s=1}^{M}\rho_p^{(s)}\rho_q^{(s)}. \tag{8b}$$

Now, for Δ_p having the probability distribution (8*a*) it is known that

$$\mathrm{Cov}(\Delta_p, \Delta_q) = [\mathbf{T}^{-1}]_{pq} \tag{9}$$

[2], and we therefore require to calculate $\mathbf{T}^{-1}$. To do this we consider the equation $\mathbf{T}f = g$ which yields

$$f_l + \sum_{s=1}^{M} \rho_l^{(s)} \sum_m{}' \rho_m^{(s)} f_m = g_l. \tag{10}$$

Multiplying this by $\rho_l^{(t)}$ and summing over l gives

$$\sum_m{}' \rho_m^{(s)} f_m = \sum_{t=1}^{M} [\mathbf{V}^{-1}]_{st} \sum_m{}' \rho_m^{(t)} g_m \tag{11a}$$

where

$$V_{st} = \delta_{st} + \sum_r{}' \rho_r^{(s)} \rho_r^{(t)}. \tag{11b}$$

Substituting from equation (11*a*) into (10) then allows f to be expressed in terms of g, the relationship yielding

$$[\mathbf{T}^{-1}]_{pq} = \delta_{pq} - \sum_{s,t=1}^{M} [\mathbf{V}^{-1}]_{st} \rho_p^{(s)} \rho_q^{(t)}. \tag{12}$$

Hence we obtain from equations (4) that

$$\mathrm{Var}(n_p) = \sigma_p^2 \left[1 - \sum_{s,t=1}^{M} [\mathbf{V}^{-1}]_{st} \rho_p^{(s)} \rho_p^{(t)} \right] \tag{13a}$$

$$\mathrm{Cov}(n_p, n_q) = -\sigma_p \sigma_q \sum_{s,t=1}^{M} [\mathbf{V}^{-1}]_{st} \rho_p^{(s)} \rho_q^{(t)} \cdot (p \neq q). \tag{13b}$$

At the expense of some straightforward (albeit possibly lengthy) manipulative algebra, equations (13) may now be applied to calculate $\mathrm{Var}(n_p)$ and $\mathrm{Cov}(n_p, n_q)$ for any given set of conservation constraints.

3. Applications

We proceed to illustrate the above approach by first applying it to the situation where only the total energy is conserved and where the number of systems can vary; this will be the case for photons or phonons obeying Bose–Einstein statistics. Here $M = 1$, with the energy conservation constraint being given by the second of equations (2). The procedure outlined in the previous paragraph can then be readily implemented as the matrix $\mathbf{V}$ has only a single element, and we finally obtain from equations (13)

$$\mathrm{Var}(n_p) = \sigma_p^2 \left[1 - \frac{\sigma_p^2 E_p^2}{\sum_m \sigma_m^2 E_m^2} \right] \tag{14a}$$

$$\mathrm{Cov}(n_p, n_q) = \frac{-\sigma_p^2 \sigma_q^2 E_p E_q}{\sum_m \sigma_m^2 E_m^2}. \tag{14b}$$

We note that $\mathrm{Var}(n_p)$ is always less than the value (σ_p^2) that it would take in the absence of the energy conservation constraint (2). This is due to the effect of this constraint in limiting possible variations of n_p; the proportional decrease in the value of $\mathrm{Var}(n_p)$ brought about by the constraint is equal to the proportional contribution of the state p to $\sum_m \sigma_m^2 E_m^2$. The energy constraint also has the effect of making $\mathrm{Cov}(n_p, n_q)$ always negative since if n_p (for specified p) is raised *above* its equilibrium value, the mean value of n_q for all other q must lie *below* the corresponding equilibrium value.

We now apply our technique to the situation considered at the outset where both number and energy are conserved corresponding to the two conservation constraints (2). The detailed implementation is straightforward, though rather more lengthy than that of the previous paragraph, and leads to

$$\mathrm{Var}(n_p) = \sigma_p^2 \left[1 - \frac{\sigma_p^2 (\sum_m \sigma_m^2 E_m^2 - 2E_p \sum_m \sigma_m^2 E_m + E_p^2 \sum_m \sigma_m^2)}{\sum_m \sigma_m^2 \sum_m \sigma_m^2 E_m^2 - (\sum_m \sigma_m^2 E_m)^2} \right] \tag{15a}$$

$$\mathrm{Cov}(n_p, n_q) = -\frac{\sigma_p^2 \sigma_q^2 [\sum_m \sigma_m^2 E_m^2 - (E_p + E_q) \sum_m \sigma_m^2 E_m + E_p E_q \sum_m \sigma_m^2]}{\sum_m \sigma_m^2 \sum_m \sigma_m^2 E_m^2 - (\sum_m \sigma_m^2 E_m)^2}. \tag{15b}$$

It may be shown that the value of $\mathrm{Var}(n_p)$ as given by (15*a*) is less than that given by (14*a*) and this corresponds to the additional effect of number conservation in limiting possible variations of n_p. On the other hand, the value of $\mathrm{Cov}(n_p, n_q)$ as given by (15*b*) is not necessarily negative; in particular if E_p and E_q are respectively sufficiently large and sufficiently small compared with the mean value of E_m, then $\mathrm{Cov}(n_p, n_q)$ will become positive. This perhaps initially surprising result that the introduction of a second conservation condition can make the covariance positive may be understood as follows. If n_p, for 'large' E_p, is raised above its equilibrium value and if n_q, for all $E_q < E_p$, is decreased below its equilibrium value in order to conserve the total number N, it will clearly not be possible to simultaneously conserve the total energy E. The only way to conserve both N and E when n_p is greater than its equilibrium value for 'large' E_p is for n_q to be less than its equilibrium value for 'intermediate' values of E_q and to be greater than its equilibrium value for 'small' values of E_q. Such a situation whereby the deviation of n_p from equilibrium has the same sign for both 'large' and 'small' E_p will lead to the possibility of $\mathrm{Cov}(n_p, n_q)$ becoming positive as described above. Finally we make the point that equations (15) can be readily shown to be equivalent to the results obtained by the Darwin–Fowler method as given in [1].

4. Conclusions

In this paper we have developed a new approach to the statistical mechanical calculation of fluctuations. Our method is simpler and more direct than that of Darwin and Fowler, and has the advantage that it may be applied to situations in which there are an arbitrary number of conserved quantities.

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