

Fluctuation
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1. Classical statistics for ideal gas

Fluctuation

$$\langle N \rangle = \int_0^\infty d\varepsilon D(\varepsilon) z e^{-\beta\varepsilon} = \frac{zV}{\lambda_{th}^3}$$
$$(\Delta N)^2 = z \frac{\partial}{\partial z} \langle N \rangle = z \frac{V}{\lambda_{th}^3} = \langle N \rangle$$

Fractional fluctuation

$$\sqrt{\frac{(\Delta N)^2}{\langle N \rangle^2}} = \frac{1}{\sqrt{\langle N \rangle}}$$

2. Fermi-Dirac statistics

Fermi-Dirac distribution function

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$$

Fluctuation:

$$(\Delta n_i)^2 = z \frac{\partial}{\partial z} \langle n_i \rangle = \langle n_i \rangle (1 - \langle n_i \rangle)$$

which is always lower than 1/4. The fluctuation for fermion is rather small. This implies that there is a repulsion force between fermions.

$$\frac{(\Delta n_i)^2}{\langle n_i \rangle^2} = \frac{1 - \langle n_i \rangle}{\langle n_i \rangle}$$

((Mathematica))

$$\text{nFD} = \frac{1}{\frac{\text{Exp}[\beta \epsilon]}{z} + 1}; \text{s3} = z \text{ D}[\text{nFD}, z] // \text{Simplify}$$

$$\frac{e^{\beta \epsilon} z}{(e^{\beta \epsilon} + z)^2}$$

$$\text{s4} = \text{nFD} (1 - \text{nFD}) // \text{Simplify}$$

$$\frac{e^{\beta \epsilon} z}{(e^{\beta \epsilon} + z)^2}$$

$$\text{s3} - \text{s4}$$

$$0$$

3. Bose-Einstein

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

$$(\Delta n_i)^2 = z \frac{\partial}{\partial z} \langle n_i \rangle = \langle n_i \rangle (\langle n_i \rangle + 1)$$

Fractional fluctuation

$$\frac{(\Delta n_i)^2}{\langle n_i \rangle^2} = \frac{\langle n_i \rangle (\langle n_i \rangle + 1)}{\langle n_i \rangle^2} = \frac{\langle n_i \rangle + 1}{\langle n_i \rangle} = 1 + \frac{1}{\langle n_i \rangle}$$

It is remarkable feature of a Boson gas that the relative fluctuations are of the order of unity for large $\langle n_i \rangle$.

((Mathematica))

$$nBE = \frac{1}{\frac{\text{Exp}[\beta \varepsilon]}{z} - 1}; s1 = z D[nBE, z] // \text{Simplify}$$

$$\frac{e^{\beta \varepsilon} z}{(e^{\beta \varepsilon} - z)^2}$$

$$s2 = nBE (nBE + 1) // \text{Simplify}$$

$$\frac{e^{\beta \varepsilon} z}{(e^{\beta \varepsilon} - z)^2}$$

$$s1 - s2$$

$$0$$

4. Fluctuation of quantum ideal gas (general)

We consider an assembly of n_k particles in the k -th quantum state. Since this set of particles is statistically independent of the remaining particles in the quantum ideal gas.

$$\begin{aligned} (\Delta N)^2 &= \langle N^2 \rangle - \langle N \rangle^2 \\ &= \langle [(N - \langle N \rangle)][(N - \langle N \rangle)] \rangle \\ &= \left\langle \sum_{k,k'} [n_k - \langle n_k \rangle][n_{k'} - \langle n_{k'} \rangle] \right\rangle \\ &= \sum_{k,k'} \langle [n_k - \langle n_k \rangle][n_{k'} - \langle n_{k'} \rangle] \rangle \\ &= \sum_{k,k'} [\langle n_k n_{k'} \rangle - \langle n_k \rangle \langle n_{k'} \rangle - \langle n_k \rangle \langle n_{k'} \rangle + \langle n_k \rangle \langle n_{k'} \rangle] \\ &= \sum_{k,k'} [\langle n_k n_{k'} \rangle - \langle n_k \rangle \langle n_{k'} \rangle] \\ &= \sum_k [\langle n_k^2 \rangle - \langle n_k \rangle^2] \\ &= \sum_k (\Delta n_k)^2 \end{aligned}$$

We note that

$$\langle N \rangle_G = \sum_k \langle n_k \rangle_G$$

$$(\Delta N)_G^2 = z \frac{\partial}{\partial z} \langle N \rangle_G = z \left(\frac{\partial \langle N \rangle}{\partial z} \right)_{V, \beta} = \sum_k z \frac{\partial}{\partial z} \langle n_k \rangle_G = \sum_k (\Delta n_k)_G^2$$

with

$$\langle n_k \rangle = \frac{1}{\frac{1}{z} e^{\beta \epsilon_k} \pm 1} \quad (+: \text{fermion}; -: \text{boson})$$

$$(\Delta n_k)^2 = z \frac{\partial}{\partial z} \langle n_k \rangle = \langle n_k \rangle (\langle n_k \rangle + 1) \quad (\text{Boson})$$

$$(\Delta n_k)^2 = z \frac{\partial}{\partial z} \langle n_k \rangle = \langle n_k \rangle (1 - \langle n_k \rangle) \quad (\text{fermion})$$

$$(\Delta n_k)^2 = \langle n_k \rangle \quad (\text{Boltzmann gas})$$

5. General formulation (Robertson)

$$U = \langle E \rangle_C = - \left(\frac{\partial}{\partial \beta} \ln Z_{CN} \right)_{V, N} = \langle E \rangle_G = - \left(\frac{\partial}{\partial \beta} \ln Z_G \right)_{V, z}$$

$$(\Delta E)_C^2 = - \left(\frac{\partial U}{\partial \beta} \right)_{V, N} = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{V, N}, \quad (\Delta E)_G^2 = - \left(\frac{\partial U}{\partial \beta} \right)_{V, z}$$

The canonical and grand canonical energy variance can be related as follows.

$$\begin{aligned}
(\Delta E)_G^2 &= -\left(\frac{\partial U}{\partial \beta}\right)_{V,z} \\
&= -\left(\frac{\partial U}{\partial \beta}\right)_{V,N} - \left(\frac{\partial \langle N \rangle}{\partial \beta}\right)_{V,z} \left(\frac{\partial U}{\partial \langle N \rangle}\right)_{V,\beta} \\
&= -\left(\frac{\partial U}{\partial \beta}\right)_{V,N} + (\Delta N)_G^2 \left[\left(\frac{\partial U}{\partial \langle N \rangle}\right)_{V,T}\right]^2
\end{aligned}$$

and

$$(\Delta N)_G^2 = z \frac{\partial \langle N \rangle}{\partial z}$$

The identities:

$$\left(\frac{\partial U}{\partial \bar{N}}\right)_T = \mu + \beta \left(\frac{\partial \mu}{\partial \beta}\right)_{\bar{N}}$$

and

$$\begin{aligned}
\left(\frac{\partial \bar{N}}{\partial \beta}\right)_z &= \left(\frac{\partial \bar{N}}{\partial \mu}\right) \left(-\frac{1}{\beta}\right) \left[\mu + \beta \left(\frac{\partial \mu}{\partial \beta}\right)_{\bar{N}}\right] \\
&= -\frac{1}{\beta} \left(\frac{\partial \bar{N}}{\partial \mu}\right) \left[\mu + \beta \left(\frac{\partial \mu}{\partial \beta}\right)_{\bar{N}}\right] \\
&= -\frac{1}{\beta} \left(\frac{\partial \bar{N}}{\partial \mu}\right) \left(\frac{\partial U}{\partial \bar{N}}\right)_T \\
&= -(\Delta N)^2 \left(\frac{\partial U}{\partial \bar{N}}\right)_T
\end{aligned}$$

where

$$\frac{\partial \bar{N}}{\partial \mu} = \beta (\Delta N)^2$$

The terms in this result are clear. The first is the energy variance attributable to heat exchange with the surroundings, but no matter flow, and the second is the additional contribution resulting from the exchange of particles between the system and its surroundings. This formula is also given in the book of Kittel (Exercise 25.6).

REFERENCES

- L.D. Landau and E.M. Lifshitz, Statistical Physics 3rd edition Part 1 [Landau and Lifshitz, Course of Theoretical Physics, vol.5] (Pergamon Press, 1980).
H.S. Robertson. Statistical Thermophysics (P T R Prentice Hall, 1993).
C. Kittel, Elementary Statistical Physics (Dover, 1986).

APPENDIX

Huang Introduction to Statistical Mechanics

For an ideal quantum gas, show that

$$\langle n_k n_p \rangle - \langle n_k \rangle \langle n_p \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_k} \langle n_p \rangle \quad (k \neq p)$$

Since $\langle n_p \rangle$ does not depend on ε_k , this gives

$$\langle n_k n_p \rangle = \langle n_k \rangle \langle n_p \rangle \quad (k \neq p)$$

((Solution))

$$\langle n_k \rangle = \frac{1}{Z_G} \sum_{\{n_1, n_2, \dots\}} n_k \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)]$$

$$Z_G = \text{or } Z_G = \sum_{\{n_1, n_2, \dots\}} \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)]$$

$$\begin{aligned} -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_p} \langle n_k \rangle &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_p} \frac{1}{Z_G} \sum_{\{n_1, n_2, \dots\}} n_k \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)] \\ &= -\frac{1}{\beta} \frac{1}{Z_G} \sum_{\{n_1, n_2, \dots\}} (-\beta n_k n_p) \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)] \\ &\quad - \frac{1}{\beta} \left(\frac{\partial}{\partial \varepsilon_p} \frac{1}{Z_G} \right) \sum_{\{n_1, n_2, \dots\}} n_k \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)] \\ &= \langle n_k n_p \rangle + \frac{1}{\beta} \left(\frac{1}{Z_G} \frac{\partial Z_G}{\partial \varepsilon_p} \right) \frac{1}{Z_G} \sum_{\{n_1, n_2, \dots\}} n_k \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots) + \beta \mu(n_1 + n_2 + \dots)] \\ &= \langle n_k n_p \rangle + \frac{1}{\beta} \left(\frac{1}{Z_G} \frac{\partial Z_G}{\partial \varepsilon_p} \right) \langle n_k \rangle \\ &= \langle n_k n_p \rangle - \langle n_k \rangle \langle n_p \rangle \end{aligned}$$

We know that $\langle n_k \rangle = \frac{1}{\frac{1}{z} e^{\beta \varepsilon_k} \pm 1}$ does not depend on ε_p . Thus the above is zero, or

$$\langle n_k n_p \rangle = \langle n_k \rangle \langle n_p \rangle \qquad (k \neq p)$$