Appendix A

FLUCTUATIONS

It is shown in Chapter 2 that certain thermodynamic properties are expressible in terms of fluctuations in the microscopic variables of a system. Here we examine the question of fluctuations from a purely thermodynamic point of view.

Consider a subsystem of macroscopic dimensions that forms part of a much larger thermodynamic system. The subsystem is assumed to be in thermal, mechanical and chemical equilibrium with the rest of the system which, being much larger, plays the role of a reservoir. The thermodynamic properties of the subsystem fluctuate around the average values characteristic of the total system, and the mean-square deviations from the average values can be derived systematically from the thermodynamic theory of fluctuations.

We assume that the total system is isolated from its surroundings. Then the probability p that a fluctuation will occur is

$$p \propto \exp(\Delta S_\mathrm{t}/k_\mathrm{B}) \tag{A.1}$$

where ΔS_t is the entropy change of the total system due to the fluctuation. Because S_t is a maximum at equilibrium, ΔS_t (< 0) will be a quadratic function of the thermodynamic variables, higher-order terms in the expansion of S_t around its maximum value being negligible for large systems. Let P, T and μ be the average pressure, temperature and chemical potential, respectively, of the reservoir. Then, given that the energy, volume and number of particles of the total system remain constant, the entropy change ΔS_t is

$$\Delta S_\mathrm{t} = \Delta S + (-\Delta U - P\Delta V + \mu\Delta N)/T \tag{A.2}$$

where ΔS, ΔU, ΔV and ΔN are the changes in thermodynamic variables of the subsystem and the second term on the right-hand side represents the entropy change of the reservoir. Since the fluctuations are very small, it is permissible to replace ΔU by an expansion in powers of ΔS, ΔV and ΔN truncated at second order, i.e.

$$\Delta U \approx T\Delta S - P\Delta V + \mu\Delta N + \tfrac{1}{2}(\Delta T\Delta S - \Delta P\Delta V + \Delta\mu\Delta N) \tag{A.3}$$

Then

$$p \propto \exp\left[-\tfrac{1}{2}\beta(\Delta T\Delta S - \Delta P\Delta V + \Delta\mu\Delta N)\right] \tag{A.4}$$

The subsystem can be defined either by the fraction of volume it occupies in the total system or by the number of particles it contains. In the second case, $\Delta N = 0$, and of the four remaining variables (P, V, T and S) only two are independent. If T and V are chosen as independent variables, and ΔS and ΔP are expressed in terms of ΔT and ΔV, (A.4) becomes

$$p \propto \exp\left(-\frac{\beta C_V}{2T}(\Delta T)^2 + \frac{\beta}{2}\left(\frac{\partial P}{\partial V}\right)_{N,T}(\Delta V)^2\right) \tag{A.5}$$

The probability that a fluctuation will occur is therefore a gaussian function of the deviations ΔT and ΔV. Equation (A.5) shows that the system is stable against fluctuations in temperature and volume provided $C_V > 0$ and $(\partial P/\partial V)_{N,T} < 0$. The mean-square fluctuations derived from (A.5) are

$$\left\langle(\Delta T)^2\right\rangle = \frac{k_B T^2}{C_V}, \qquad \left\langle(\Delta V)^2\right\rangle = -k_B T\left(\frac{\partial V}{\partial P}\right)_{N,T} = V k_B T \chi_T \tag{A.6}$$

while $\langle \Delta T \Delta V \rangle = 0$. Fluctuations in temperature are therefore independent of those in volume. Alternatively, choice of S and P as independent variables transforms (A.4) into

$$p \propto \exp\left(-\frac{1}{2k_B C_P}(\Delta S)^2 + \frac{\beta}{2}\left(\frac{\partial V}{\partial P}\right)_{N,S}(\Delta P)^2\right) \tag{A.7}$$

where C_P is the heat capacity at constant pressure. The averages calculated from (A.7) are

$$\left\langle(\Delta S)^2\right\rangle = k_B C_P, \qquad \left\langle(\Delta P)^2\right\rangle = -k_B T\left(\frac{\partial P}{\partial V}\right)_{N,S} = \frac{k_B T}{V \chi_S} \tag{A.8}$$

where $\chi_S = -(1/V)(\partial V/\partial P)_{N,S}$ is the adiabatic compressibility, and $\langle \Delta S \Delta P \rangle = 0$. Fluctuations in entropy are therefore independent of those in pressure.

Finally, if the subsystem is defined as occupying a fixed fraction of the total volume, the mean-square fluctuation in the number of particles in the subsystem can be calculated, with the help of (2.4.22), to be

$$\left\langle(\Delta N)^2\right\rangle = k_B T\left(\frac{\partial N}{\partial \mu}\right)_{V,T} = \rho N k_B T \chi_T \tag{A.9}$$

Equation (A.9) is identical to the statistical mechanical relation relation (2.4.23), while comparison of (A.9) with (A.6) shows that volume fluctuations at constant N are equivalent to number fluctuations at constant V.