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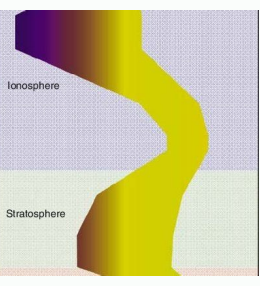
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2.2 Answers

• **Problem 2.1** Consider a system whose volume V is fixed, and which is brought into contact with a heat bath at temperature T . As long as the system is not in equilibrium with the bath, it cannot be assigned a definite temperature, so its Helmholtz free energy F is not a well-defined function of temperature and volume. We may, however, attempt to define a non-equilibrium free energy by

$$F = U - TS.$$

Here, we understand by U the internal energy of the system, which is well defined even away from equilibrium, and by T the temperature of the heat bath, (which will also be the temperature of the system once equilibrium is attained). The non-equilibrium entropy S of the system is not simply a function of U and V but depends on details of the non-equilibrium state. We can appeal to Clausius' statement of the second law to write the inequality

$$\delta S \geq \delta Q/T$$

where δQ is an amount of heat transferred from the heat bath to the system. Since the volume of the system is constant, no work is done while this heat is transferred, so the change in the system's internal energy is $\delta U = \delta Q$. Since the temperature T of the heat bath is fixed, we deduce that

$$\delta F = \delta U - T \delta S = \delta Q - T \delta S \leq 0.$$

Thus, F always decreases as the system approaches equilibrium and reaches a minimum when equilibrium is attained.

In the case of the Gibbs free energy $G = U + PV - TS$, we must consider a system whose pressure P is held fixed, but whose volume is allowed to vary as it approaches equilibrium. In this case, changes in energy are given by $\delta U = \delta Q - P \delta V$. An argument similar to that given above yields

$$\delta G = \delta U + P \delta V - T \delta S = \delta Q - T \delta S \leq 0.$$

Note that F is useful for describing a system whose temperature and volume are subject to external control, whereas G is more useful when the temperature and pressure are externally controlled.

• **Problem 2.2** Consider a system of bounded energy. That is, the system has both a lowest possible energy, which we can take to be $U = 0$, and a greatest possible energy, say U_{max} . For such a system, it is likely that very few microstates (perhaps only one) correspond to $U = 0$, and also that very few correspond to $U = U_{max}$. Thus, the entropy $S(U)$ is very small both at $U = 0$ and at $U = U_{max}$, and there is some intermediate energy U^* at which $S(U)$ is a maximum. The inverse temperature $T^{-1} = \partial S/\partial U$ is zero

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