Simple Systems without Interactions

2.1. INTRODUCTION

In this chapter we present some applications of ST to very simple systems. The simplicity here arises from either negligible or total absence of interparticle interactions. Lack of interaction usually implies independence of the particles. This, in turn, leads to a relatively easy solution for the PF of the system. A total lack of interactions never exists in real systems. Nevertheless, such idealized systems are interesting for two reasons. First, some systems behave, to a good approximation, as if there are no interactions (e.g., a real gas at very low densities, adsorption of molecules on sites that are far apart). Second, real systems with interactions can be viewed and treated as extensions of idealized simple systems. For instance, the theory of real gases is based on corrections due to interactions between pairs, triplets, etc. Even in the very simple systems, some interactions between particles or between particles and an external field are essential to the maintenance of equilibrium. Lack of interactions usually leads to solvability of the PF, but this is not always so. In Chapter 3 we shall study systems with interactions among a small number of particles for which a PF can be written explicitly. Likewise, the inherent simplicity of the one-dimensional systems studied in Chapter 4 also leads to solvability of the PF.

2.2. THE CHEMICAL POTENTIAL OF AN IDEAL GAS

In section 1.6 we derived the thermodynamic quantities of an ideal gas. Of particular importance is the chemical potential, which is now written as

\[ \mu = kT \ln q^{-1} + kT \ln \frac{N}{V} \Lambda^3. \]  \hspace{1cm} (2.2.1)

Here, \( q \) is the internal partition function of a single molecule, \( V \) the volume of the system, \( N \) the number of particles, and \( \Lambda^3 \) the momentum partition function.

It is convenient to assign meaning to the two terms in (2.2.1) as follows: the chemical potential is defined, in the \( T, V, N \) ensemble, as

\[ \mu = \left( \frac{\partial A}{\partial N} \right)_{T,V} = A(T, V, N + 1) - A(T, V, N), \]  \hspace{1cm} (2.2.2)

where the second equality follows from the extensive property of the Helmholtz energy and the fact that the addition of one particle to a macroscopic system can be viewed as an infinitesimal change in the variable \( N \).
Suppose that instead of just adding one particle to the system, we introduce the particle at a fixed position in the system, say, at \( \mathbf{r}_0 \). The corresponding change in the Helmholtz energy is defined by

\[
\mu^* = A(T, V, N + 1, \mathbf{r}_0) - A(T, V, N)
\]

\[
= -kT \ln \left[ \frac{q^{N + 1} V^N}{\Lambda^N N!} \right] + kT \ln \left[ \frac{q^N V^N}{\Lambda^N N!} \right] = kT \ln q^{-1}. \tag{2.2.3}
\]

We see that this quantity is equal to the first term on the rhs of (2.2.1). We shall refer to \( \mu^* \) as the pseudo chemical potential.

Combining (2.2.1) with (2.2.3), we obtain

\[
\mu = \mu^* + kT \ln \frac{N}{V} \Lambda^3. \tag{2.2.4}
\]

Thus the work required to introduce one particle into the system is divided into two parts, of which the first is the work required to place the particle at a fixed position in the system. Next the particle is freed; the corresponding work is \( kT \ln \rho \Lambda^3 \). We shall refer to this term as the liberation Helmholtz energy. It is easy to show that the corresponding liberation Gibbs energy has the same form as in (2.2.4) with the replacement of \( V \) by the average volume in the \( T, P, N \) ensemble (see Appendix E).

When the particle is released from its fixed position, there are three sources of the change in the Helmholtz energy. First, it can acquire translational kinetic energy, the corresponding contribution being \( kT \ln \Lambda^3 \). Second, the particle can now wander in the entire volume \( V \), the corresponding contribution being \(-kT \ln V \). Finally, when the particle is at a fixed position, it is distinguishable from all the \( N \) indistinguishable particles. This is the reason for having \( N! \) in both terms on the rhs of (2.2.3). Once the particle is released, it is no longer distinguishable from other members of the same species. We shall refer to the term \( kT \ln \frac{N}{V} \Lambda^3 \) as being due to the assimilation of one particle by \( N \) indistinguishable particles. Together the three contributions give rise to the liberation term \( kT \ln \rho \Lambda^3 \), where \( \rho \Lambda^3 \) is a dimensionless quantity. Note that since we are using classical ST, \( \rho \Lambda^3 < 1 \); therefore the liberation Helmholtz energy is always negative.

Each of the factors mentioned above can be changed independently. If we change the temperature (at \( V, N \) constant), the change in the chemical potential is

\[
\mu(T_2) - \mu(T_1) = \mu^*(T_2) - \mu^*(T_1) + kT_2 \ln \Lambda^3(T_2) - kT_1 \ln \Lambda^3(T_1). \tag{2.2.5}
\]

On the other hand, at a fixed temperature we may change the volume, say from \( V \) to \( 2V \); the corresponding change of the chemical potential is

\[
\mu(2V) - \mu(V) = kT \ln \frac{V}{2V} = kT \ln \frac{1}{2}. \tag{2.2.6}
\]

The change in the chemical potential for the expansion process is negative. Finally, we can change \( N \) and keep \( T \) and \( V \) constant, for instance, by eliminating \( \frac{1}{2}N \) of the particles. The corresponding change in the chemical potential is

\[
\mu\left(\frac{1}{2}N\right) - \mu(N) = kT \ln \frac{N}{2N} = kT \ln \frac{1}{2}. \tag{2.2.7}
\]