External Parameters

So far, we were characterizing an equilibrium state by only one thermodynamic variable: either $T$, or $E$, or $S$, etc. Fixing one of these variables, say, $E$, we could (at least in principle) express the rest of them as functions: $S(E)$, $T(E)$, etc., because all the variables were related to each other through the Gibbs distribution. Incidentally, the functions $S(E)$, $T(E)$, $E(T)$, $S(T)$, etc., are called equations of state of a given system. There are, however, other natural parameters which the state of the system can depend on—the system volume, or/and the value of applied magnetic or electric field, inter-particle interaction, and so on. In this case, the Gibbs distribution and, correspondingly, the equations of state will also include these variables. Previously we simply kept all these parameters fixed. Now we are going to let them vary.

There is a general relation between small variations of energy, entropy, and any external parameter $\lambda$, which follows from the formula

$$E = F + TS.$$  \hspace{1cm} (1)

Eq. (1) is valid in any equilibrium state. Hence if we consider an infinitesimal variation of the state—from one equilibrium into another equilibrium—the differentials $dE$, $dF$, $dT$, and $dS$ should be related by

$$dE = dF + T dS + S dT.$$  \hspace{1cm} (2)

By its definition, the Helmholtz free energy $F$ is naturally expressed as a function of $T$ and $\lambda$:

$$F(T, \lambda) = -T \ln \left( \sum_n e^{-E_n(\lambda)/T} \right).$$  \hspace{1cm} (3)

[Note that the only place where the dependence on $\lambda$ comes from is the position of the $n$-th energy level.] For any function of two variables, from Calculus we have

$$dF = \frac{\partial F(T, \lambda)}{\partial T} dT + \frac{\partial F(T, \lambda)}{\partial \lambda} d\lambda.$$  \hspace{1cm} (4)

Previously, we have established that

$$\frac{\partial F(T, \lambda)}{\partial T} = -S.$$  \hspace{1cm} (5)

[We were differentiating $F$ with respect to $T$ assuming that all the external parameters are fixed, which exactly corresponds to the meaning of this partial derivative.] Hence,

$$dF = -S dT + \frac{\partial F(T, \lambda)}{\partial \lambda} d\lambda.$$  \hspace{1cm} (6)

Plugging this into (2), we get the desired relation:

$$dE = T dS + \frac{\partial F(T, \lambda)}{\partial \lambda} d\lambda.$$  \hspace{1cm} (7)

We see that the partial derivative $\partial F(T, \lambda)/\partial \lambda$ plays an important thermodynamic role. Below we will reveal an explicit physical meaning of this quantity in the case when $\lambda$ is the system volume.
Pressure. Generalized force

How do we generically define pressure? We say that the pressure is a force per unit area. This definition needs to be further developed for the case of a quantum system, where the force is not a natural quantum mechanical observable.

Consider a piston of the area \( A \) squeezing some quantum system. To keep the volume fixed, we need to apply some external force \( F \) which in the case of a macroscopic system turns out to be proportional to \( A \):

\[
F = PA.
\]

The proportionality coefficient \( P \) is called pressure. To relate \( P \) to the microscopic characteristics of our system, we perform the following gedanken experiment. We shift the piston by some small distance \( \Delta x \) along the \( x \) axis. Then, the work \( \Delta W \) performed by the external force \( F \) is given by

\[
\Delta W = F \Delta x = PA \Delta x = -P \Delta V,
\]

where \( \Delta V \) is the change of volume. We also assume that our system is thermally isolated and thus the conservation of energy simply implies

\[
\Delta W = \Delta E,
\]

where \( E \) is the system energy. Hence, for the pressure we have

\[
P = -\lim_{\Delta V \to 0} \frac{\Delta E}{\Delta V}.
\]

One can introduce a quantum mechanical operator of pressure by noting that energy is the expectation value of the Hamiltonian \( H \). Hence, it is natural to expect that the operator of pressure is

\[
\hat{P} = -\lim_{\Delta V \to 0} \frac{\Delta H}{\Delta V} = -\frac{\partial H}{\partial V}.
\]

(Below we present a rigorous derivation of this formula.)

To calculate the pressure for a thermodynamically equilibrium system we need to find the expectation value of this operator with respect to Gibbs distribution:

\[
P = \sum_n w_n \langle n|\hat{P}|n \rangle = \sum_n w_n \langle n|\frac{\partial H}{\partial \lambda}|n \rangle.
\]

Next steps are generic. If the Hamiltonian \( H \) depends on some external parameter \( \lambda \), then for the quantity

\[
\langle n|\frac{\partial H}{\partial \lambda}|n \rangle = \frac{\partial}{\partial \lambda} \langle n|H|n \rangle = \frac{\partial E_n}{\partial \lambda},
\]

we proceed as follows. First, we observe that

\[
\langle n|\frac{\partial H}{\partial \lambda}|n \rangle = \frac{\partial}{\partial \lambda} \langle n|H|n \rangle = \frac{\partial E_n}{\partial \lambda}.
\]

Indeed,

\[
\frac{\partial}{\partial \lambda} \langle n|H|n \rangle = \langle \frac{\partial}{\partial \lambda} \psi_n|H|\psi_n \rangle = \langle \frac{\partial}{\partial \lambda} \psi_n|H|\psi_n \rangle + \langle \psi_n|\frac{\partial H}{\partial \lambda}|\psi_n \rangle + \langle \psi_n|H|\frac{\partial}{\partial \lambda} \psi_n \rangle =
\]

\[
E_n \langle \frac{\partial}{\partial \lambda} \psi_n|\psi_n \rangle + \langle \psi_n|\frac{\partial H}{\partial \lambda}|\psi_n \rangle + E_n \langle \psi_n|\frac{\partial}{\partial \lambda} \psi_n \rangle = E_n \langle \frac{\partial}{\partial \lambda} \psi_n|\psi_n \rangle + E_n \langle \psi_n|\frac{\partial H}{\partial \lambda}|\psi_n \rangle.
\]

But \( \langle \psi_n|\psi_n \rangle \equiv 1 \) by normalization, and any derivative from it is identically equal to zero.
Hence,
\[ \langle \frac{\partial H}{\partial \lambda} \rangle = \sum_n w_n \frac{\partial E_n}{\partial \lambda}. \] (17)

Then we differentiate the partition function with respect to \( \lambda \), temperature being fixed:
\[ \left( \frac{\partial Z}{\partial \lambda} \right)_T = \frac{\partial}{\partial \lambda} \sum_n e^{-E_n/T} = -\frac{1}{T} \sum_n e^{-E_n/T} \frac{\partial E_n}{\partial \lambda} = -\frac{Z}{T} \sum_n w_n \frac{\partial E_n}{\partial \lambda}, \] (18)

and thus find that
\[ \langle \frac{\partial H}{\partial \lambda} \rangle = -\frac{T}{Z} \left( \frac{\partial Z}{\partial \lambda} \right)_T = \left( \frac{\partial F}{\partial \lambda} \right)_T. \] (19)

Replacing now \( \lambda \to V \), we get the formula
\[ P = -\frac{\partial F(T,V)}{\partial V}. \] (20)

With this result, the relations (6) and (7), yield
\[ dF = -SdT - PdV, \] (21)
\[ dE = TdS - PdV. \] (22)

Note also that in a general case, Eq. (19) allows us to write Eqs. (6)-(7) as
\[ dF = -SdT + \langle \frac{\partial H}{\partial \lambda} \rangle d\lambda, \] (23)
\[ dE = TdS + \langle \frac{\partial H}{\partial \lambda} \rangle d\lambda. \] (24)

There is a subtlety about the operator of pressure. Namely, we were taking for granted that \( \Delta E \) was independent of the protocol of producing corresponding small change in volume. Now we elaborate on this issue.

Let the Hamiltonian depend on time through some time-dependent parameter \( \lambda(t) \). [In the case of pressure, \( \lambda \equiv V \).] Consider the (time-dependent) quantum mechanical expectation of energy
\[ E(t) = \langle \psi(t)|H(t)|\psi(t) \rangle \] (25)
and differentiate it with respect to time:
\[ \dot{E} = \langle \psi(t)|H|\psi(t) \rangle + \langle \psi|\frac{\partial H}{\partial t}|\psi \rangle + \langle \psi|H|\frac{\partial \psi}{\partial t} \rangle. \] (26)

Taking into account Schrödinger equation
\[ i\hbar \frac{\partial \psi}{\partial t} = H\psi, \] (27)
we notice that
\[ \langle \frac{\partial \psi}{\partial t}|H|\psi \rangle + \langle \psi|H|\frac{\partial \psi}{\partial t} \rangle = (i/\hbar) \langle \psi|H^2|\psi \rangle - (i/\hbar) \langle \psi|H^2|\psi \rangle = 0, \] (28)
and thus
\[ \dot{E} = \langle \psi|\frac{\partial H}{\partial t}|\psi \rangle. \] (29)
The dependence of $H$ on $t$ comes through $\lambda(t)$. That is

$$\frac{\partial H}{\partial t} = \dot{\lambda} \frac{\partial H}{\partial \lambda}. \quad (30)$$

Plugging this into Eq. (29), we conclude that

$$\dot{E} = \langle \psi | \frac{\partial H}{\partial \lambda} | \psi \rangle \dot{\lambda}, \quad (31)$$

or, equivalently,

$$dE = \langle \psi | \frac{\partial H}{\partial \lambda} | \psi \rangle d\lambda. \quad (32)$$

This is the crucial result saying that if the variation of $\lambda$ is small enough, then the corresponding variation of energy is defined only by the state $\psi$ and the variation of $\lambda$, the time-dependence of $\lambda$ being irrelevant. Moreover, variation of energy is proportional to the variation of $\lambda$, the proportionality coefficient—generalized force—being given by the expectation value of the following operator

$$\mathcal{F} = \frac{\partial H}{\partial \lambda}, \quad (33)$$

which we refer to as the operator of generalized force.

**Work and Heat**

**The First Law of Thermodynamics**

Suppose the system energy has been changed by a certain amount $\Delta E$. Since the total energy is conserved, $\Delta E$ should be equal to the sum of energies taken from other systems either in the form of *heat* (the energy associated with chaotic microscopic motions) or in the form of *mechanical work*, or both. Hence, for a thermodynamic processes with a given system the conservation of energy can be written as

$$\Delta E = \Delta Q + \Delta W, \quad (34)$$

where $\Delta Q$ is the portion of energy transferred to the system in the form of heat, while $\Delta W$ is the energy transferred in the form of mechanical work. Eq. (34) is known as the first law of thermodynamics.

**Heat and Entropy**

Eq. (34) is always true, since it is just the law of energy conservation. Consider now a quasi-equilibrium process, that is a process when temporal variations of parameters are slow enough so that the evolution is just a chain of equilibrium states. In this case, we can use the equilibrium relations established in the previous section. In particular, we have

$$dE = T dS - P dV, \quad (35)$$

which implies that

$$\Delta E \approx T \Delta S - P \Delta V, \quad (36)$$
if all $\Delta$’s are small enough. Comparing (36) and (34), with (9) taken into account, we come to a fundamental relation between the heat transfer, entropy change, and temperature:

$$\Delta Q = T \Delta S \quad (\Delta Q \rightarrow 0).$$

Introducing a pseudo-differential $dQ$ standing for an infinitesimal amount of transferred heat, we write (37) as

$$dS = \frac{dQ}{T}.$$  \hspace{1cm} (38)

One can employ this relation for an experimentally measuring the entropy. Indeed, starting from some very low temperature $T_0$, where the entropy is almost zero, and adding energy to the system of interest in the form of heat by small enough portions, and keeping track of the temperature, one gets the entropy in the form of the following integral (sum) over the experimental data:

$$S(T_n) = \int \frac{dQ}{T} \approx \frac{\Delta Q_0}{T_0} + \frac{\Delta Q_1}{T_1} + \ldots + \frac{\Delta Q_n}{T_n} \quad (n \gg 1).$$

In an essentially non-equilibrium process there is an extra increase of entropy due to relaxation processes. (We have established this fact previously by considering two systems with different temperatures relaxing towards some common temperature.) In this case instead of (37) we have

$$\Delta S > \frac{\Delta Q}{T} \quad \text{(non-equilibrium process)}.$$

As we will show later, this thermodynamic inequality leads to an upper bound of the efficiency of heat machines.

### Adiabatic Process

Suppose our system is isolated from any heat baths and we slowly change some external parameter $\lambda$ (say, volume or magnetic field) so that the process is quasi-equilibrium. Such a process is called adiabatic. The word ‘adiabatic’ is just a term for ‘quasi-equilibrium and thermally isolated’. Because of the quasi-equilibrium character of the process, we can use Eq. (38), while the fact that the system is thermally isolated means that there is no heat transfer: $dQ = 0$. We conclude that in adiabatic process entropy remains constant. And this allows us to relate the temperature to the particular value of the parameter $\lambda$ by an implicit function

$$S(T, \lambda) = S(T_0, \lambda_0),$$

where $T_0$ and $\lambda_0$ are the initial values of $T$ and $\lambda$. The curve $T(\lambda)$ specified by Eq. (41) is called adiabat.

**Problem 22.** A macroscopic system of almost non-interacting spins-1/2 (of one and the same magneton) is in an external magnetic field. The system is thermally isolated and is in equilibrium. The external magnetic field is adiabatically decreased by a factor of 100. What happens to the temperature?

### Heat Capacities

Most generally, by heat capacity we mean the heat required for a unit change in the temperature of a body. Hence, to obtain the heat capacity we need to find the limit of the ratio $\Delta Q/\Delta T$ as $\Delta T \rightarrow 0$. In case when the state of a system depends not only on the temperature, but also on some other quantities, like volume or pressure, this definition of heat capacity is ambiguous. For example, if we change the temperature of water in a glass (open surface), then the volume changes as well due to
the expansion of the liquid, while the pressure remains constant. Alternatively, if we heat up water in a closed container with rigid walls, the volume remains constant. Hence, the value of heat capacity may depend on the character of a process, and to fix the definition, we need to specify the parameter (set of parameters), $\xi$, that is (are) kept constant when we add heat to the system. We thus write

$$C_\xi = \lim_{\Delta T \to 0, \xi = \text{const}} \frac{\Delta Q}{\Delta T}.$$  \hspace{1cm} (42)$$

Eq. (37) states that this is equivalent to

$$C_\xi = T \lim_{\Delta T \to 0, \xi = \text{const}} \frac{\Delta S}{\Delta T} \equiv T \left( \frac{\partial S}{\partial T} \right)_\xi.$$  \hspace{1cm} (43)$$

For the two most typical heat capacities, $C_V$ and $C_P$, we have:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V, \hspace{1cm} C_P = T \left( \frac{\partial S}{\partial T} \right)_P.$$  \hspace{1cm} (44)$$