that the probability of observing the system alone with energy E and particle number N is proportional to $e^{-\frac{(E-\mu N)}{kT}}$. In addition to the average energy of the system, the average particle number is now fixed and is controlled by the chemical potential μ.

The thermodynamic limit for a physical system of N particles contained in a volume V is defined by taking the limit as N and V go to infinity such that the ratio $\rho = \frac{N}{V}$ remains constant. An essential result of thermodynamics is that the three ensembles are equivalent for describing the macroscopic properties of most system in the thermodynamic limit. One is then free to select the ensemble on the basis of formal convenience, and as in the case of classical statistical mechanics, the grand canonical ensemble offers the greatest formal simplicity.

The principal case in which the three ensmbles yield nonequivalent results arises when some observable has divergent fluctuations in one ensemble and is constrained not to fluctuate in another ensemble. This situation occurs in physical systems composed of a mixture of phases such as a liquid-gas transition or Bose condensation. If one looks at a subsystem, the fact that droplets of one phase can move in the other phase is responsible for the divergence of the fluctuations of the particle number in the grand canonical ensemble, whereas these fluctuations are zero by definition in the canonical ensemble.

Given the fact that the probability of observing a state of energy E and particle number N is proportional to $e^{-\beta(E-\mu N)}$, where $\beta = \frac{1}{kT}$, the thermal average of an operator $\hat{R}$ may be expressed as

$$\langle \hat{R} \rangle = \frac{\sum_\alpha \langle \psi_\alpha | e^{-\beta(\hat{H}-\mu\hat{N})} \hat{R} | \psi_\alpha \rangle}{\sum_\alpha \langle \psi_\alpha | e^{-\beta(\hat{H}-\mu\hat{N})} | \psi_\alpha \rangle} \tag{2.1}$$

where $\{|\psi_\alpha\rangle\}$ denotes an orthonormal basis of the Fock space and $\hat{N}$ is the particle number operator, Eq. (1.92). It is convenient to define the partition function, Z,

$$Z = \text{Tr}\, e^{-\beta(\hat{H}-\mu\hat{N})} \tag{2.2}$$

and the grand canonical potential, Ω

$$e^{-\beta\Omega} = Z \ . \tag{2.3}$$

By explicit differentiation of the function $\Omega(\mu, V, T)$ and use of Eqs. (2.1–2.3) the familiar thermodynamic relations may be established:

$$\frac{\partial\Omega}{\partial\mu} = -N \tag{2.4a}$$

$$\frac{\partial\Omega}{\partial V} = -P \tag{2.4b}$$

$$\frac{\partial\Omega}{\partial T} = \frac{\Omega - \mathcal{U} - \mu N}{T} = -S \tag{2.4c}$$

where P is the pressure, $\mathcal{U}$ is the internal energy, and S is the entropy. The Gibbs-Duhem relation

$$\mathcal{U} = TS - PV + \mu N \tag{2.5}$$

follows from the fact that the internal energy $\mathcal{U}(N, V, S)$ is an extensive function of extensive variables and may be combined with Eq. (2.4c) to yield

$$\Omega = -PV \ . \tag{2.6}$$

Since the thermodynamic properties of a system at equilibrium are specified by Ω and derivatives thereof, one of the immediate tasks in this chapter will be to develop methods to calculate the grand potential, Ω. The techniques developed for Ω will also apply directly to thermal averages of operators, Eq. (2.1), allowing the calculation of any equilibrium properties of interest.

PHYSICAL RESPONSE FUNCTIONS AND GREEN'S FUNCTIONS

Before embarking on the development of the general formalism, it is valuable to specify conveniently calculable quantities which characterize the range of experimentally accessible observables to be addressed in physical systems. In addition to measuring the equilibrium properties discussed above, experimentalists learn about physical systems by measuring their response to a diversity of external probes. The results of such measurements are conveniently expressed in terms of response functions or Green's functions. The relation of specific experimental observables to these quantities will be derived in detail in later chapters, and in the present section we simply present general arguments to show how they arise naturally from experiments.

Consider a system which at initial time t_i is in an eigenstate $|\Psi_\alpha(t_i)\rangle$ of the hamiltonian $\hat{H}$. Subsequently, let it be subject to a time-dependent external field

$$\hat{H}_U(t) = \hat{H} + U(t)\hat{O}_1 \tag{2.7}$$

where the field couples to the system through an operator denoted $\hat{O}_1$ and the states and operators are in the Schrödinger representation.

A convenient representation of the evolution operator for a system with a time-dependent hamiltonian is given by a time-ordered exponential. The time-ordered product of a set of time-dependent creation and annihilation operators, denoted $\{O_\alpha\}$, is defined

$$T[O_{\alpha_1}(t_1)O_{\alpha_2}(t_2)\dots O_{\alpha_n}(t_n)] = \varsigma^P O_{\alpha_{P1}}(t_{P1})O_{\alpha_{P2}}(t_{P2})\dots O_{\alpha_{Pn}}(t_{Pn}) \tag{2.8}$$

where according to our standard convention ς is -1 or 1 for Fermions or Bosons respectively and P is the permutation of $\{1, 2, \dots n\}$ which orders the times chronologically with the latest time to the left:

$$t_{P1} > t_{P2} > \dots > t_{Pn}$$

and which orders creation operators to the left of annihilation operators (normal order) at equal times. The time-ordered exponential is defined by

$$T\, e^{-\int_{t_a}^{t_b} dt A(t)} = \lim_{M\to\infty} e^{-\epsilon A(t_M)} e^{-\epsilon A(t_{M-1})} \dots e^{-\epsilon A(t_1)} e^{-\epsilon A(t_0)} \tag{2.9}$$

where $\epsilon = \frac{t_b - t_a}{M}$ and $t_n = t_a + n\epsilon$. As shown in Problem 2.3, it may be expanded in a Taylor series as follows:

$$T\; e^{-\int\limits_{t_a}^{t_b} dt\, A(t)} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int\limits_{t_a}^{t_b} dt_1 \ldots dt_n T[A(t_1) \ldots A(t_n)] \; . \qquad (2.10)$$

Using this time-ordered exponential, the evolution operator may be written

$$\hat{U}(t, t_i) = T\; e^{-i\int_{t_i}^{t} \hat{H}_U(t')dt'} \qquad (2.11)$$

since it satisfies the equation of motion

$$\frac{d}{dt}\hat{U}(t, t_i) = T(-i\hat{H}_U(t)\; e^{-i\int_{t_i}^{t} \hat{H}_U(t')dt'})$$
$$- i\hat{H}_U(t)\hat{U}(t, t_i) \qquad (2.12a)$$

and the boundary condition

$$\hat{U}(t_i, t_i) = 1 \; . \qquad (2.12b)$$

The response of a wave function originally in eigenstate $|\psi_\alpha\rangle$ at time t_i to an infinitesimal perturbation by an external field acting between time t_i and t is thus given by the functional derivative

$$\delta|\psi(t)\rangle = \int_{t_i}^{t} dt_1 \delta U(t_1) \left.\frac{\delta \hat{U}(t, t_i)}{\delta U(t_1)}\right|_{U=0} |\psi_\alpha(t_i)\rangle$$
$$= -i\int_{t_i}^{t} dt_1 \delta U(t_1) T e^{-i\int_{t_1}^{t} \hat{H}_U(t')dt'} \mathcal{O}_1 T\; e^{-i\int_{t_i}^{t_1} \hat{H}_U(t')dt'}\Big|_{U=0} |\psi_\alpha(t_i)\rangle$$
$$= -i\int_{t_i}^{t} dt_1 \delta U(t_1) e^{-iH(t-t_1)} \mathcal{O}_1 e^{-iH(t_1-t_i)} |\psi_\alpha(t_i)\rangle$$
$$= -i\int_{t_1}^{t} dt_1 \delta U(t_1) e^{-iHt} \mathcal{O}_1^{(H)}(t_1) |\psi_\alpha^{(H)}\rangle$$

$$(2.13)$$

where the operator $\mathcal{O}_1^{(H)}(t)$ in the Heisenberg representation is related to the operator $\mathcal{O}_1$ in the Schrödinger representation by

$$\mathcal{O}_1^{(H)}(t) \equiv e^{iHt}\mathcal{O}_1\; e^{-iHt} \qquad (2.14a)$$

and the state $|\psi^{(H)}\rangle$ in the Heisenberg representation is related to the state $|\psi(t)\rangle$ in the Schrödinger representation by

$$|\psi^{(H)}\rangle \equiv e^{iHt} |\psi(t)\rangle \; . \qquad (2.14b)$$

Finally, consider the expectation value of an operator $\mathcal{O}_2$ evaluated at time t_2 in the state $|\psi(t_2)\rangle$. The response of this expectation value to an infinitesimal perturbation in the external field is given by

$$\delta\langle\psi(t_2)|\hat{\mathcal{O}}_2|\psi(t_2)\rangle = -i\int_{t_i}^{t_2} dt_1 \delta U(t_1)\langle\psi_\alpha^{(H)}|\left[\hat{\mathcal{O}}_2^{(H)}(t_2), \hat{\mathcal{O}}_1^{(H)}(t_1)\right]|\psi_\alpha^{(H)}\rangle$$
$$= -i\int_{-\infty}^{\infty} dt_1 \delta U(t_1)\theta(t_2 - t_1)\langle\psi_\alpha^{(H)}|\left[\hat{\mathcal{O}}_2^{(H)}(t_2), \hat{\mathcal{O}}_1^{(H)}(t_1)\right]|\psi_\alpha^{(H)}\rangle$$

$$(2.15)$$

where a θ function has been inserted to extend the upper limit of the time integral and the lower limit t_i has been extended to $-\infty$ to include all possible variations of $U(t_1)$. This equation may be weighted by the Boltzmann factor $Z^{-1} e^{-(E_\alpha - \mu N_\alpha)}$ and summed over a complete set $\{\alpha\}$. Hence, the response of a measurement of $\langle\hat{\mathcal{O}}_2(t_2)\rangle$ to a perturbation coupled to $\hat{\mathcal{O}}_1$ is specified by the response function

$$D(1, 2) \equiv \frac{\delta\langle\hat{\mathcal{O}}_2(t_2)\rangle}{\delta U(t_1)}$$
$$= -i\theta(t_2 - t_1)\langle[\hat{\mathcal{O}}_2^{(H)}(t_2), \hat{\mathcal{O}}_1^{(H)}(t_1)]\rangle$$

$$(2.16)$$

where the brackets denote the thermal average, Eq. (2.1).

The physical response of a system to an external potential is thus characterized by correlation functions of the form $\langle\hat{\mathcal{O}}_2^{(H)}(t_2)\hat{\mathcal{O}}_1^{(H)}(t_1)\rangle$. This result that a transport coefficient characterizing the dissipation in a system is specified by a matrix element of the thermodynamic or ground state fluctuations of an operator is often called the fluctuation-dissipation theorem. For example consider measuring the magnetization of a spin system in the presence of a time and spatially varying magnetic field. Since the magnetic field couples to the spin through $\vec{\hat{\sigma}}(x) \cdot \vec{H}(x)$, the operators $\hat{\mathcal{O}}_1$ and $\hat{\mathcal{O}}_2$ are spin operators $\vec{\hat{\sigma}}$ and the response function is given in terms of the spin-spin correlation function $\langle\vec{\hat{\sigma}}(x_1, t_1)\vec{\hat{\sigma}}(x_2, t_2)\rangle$. Fourier transforming to momentum and frequency then directly specifies the dynamic magnetic susceptibility $\chi(k, \omega)$. Similarly, an electromagnetic field couples to a system of charged particles though the vector potential $\vec{\hat{j}} \cdot \vec{A}$, and in a gauge in which $\Phi = 0, \vec{E} = -\frac{\partial}{\partial t}\vec{A}$. Thus, the response of the current to a variation in the electric field, that is the electrical conductivity, is given by the current-current correlation function $\langle\vec{\hat{j}}(x_1, t_1)\;\vec{\hat{j}}(x_2, t_2)\rangle$. This argument is evidently quite general, and a large class of experiments in which a system is subjected to a weak controllable external probe is characterized by simple correlation functions of operators at different times.

In addition to these experiments involving an external potential, there is an important class of inclusive scattering experiments used to study many-body systems which may be characterized similarly by correlation functions. Consider an external particle which interacts with the constituents of a system through a weak potential v. Let a particle with initial momentum $\vec{k}$ scatter from the system in initial state $|\psi_\alpha\rangle$ transferring energy ω and momentum $\vec{q}$ leading to a final state $|\psi_\beta\rangle$ and final particle

momentum $\vec{k} - \vec{q}$. The matrix element for this transition is

$$
\begin{aligned}
T_{\alpha\beta} &= \int dx_1 \ldots dx_n dx \psi_\beta^*(x_1, \ldots x_n) e^{-i(\vec{k}-\vec{q})\cdot\vec{x}} \sum_i v(x - x_i) e^{i\vec{k}\cdot\vec{x}} \psi_\alpha(x_1 \ldots x_n) \\
&= \int dx dy e^{i\vec{q}\cdot\vec{x}} v(x - y) |\langle\psi_\beta|\hat{\rho}(y)|\psi_\alpha\rangle \\
&= \tilde{v}(-q)\langle\psi_\beta|\hat{\rho}(-q)|\psi_\alpha\rangle
\end{aligned}
\tag{2.17}
$$

where $\tilde{v}(q) = \tilde{v}(-q)$ is the Fourier transform of the potential $v(|x|)$ and the Fourier transform of the density operator is defined by

$$
\hat{\rho}(k) = \int e^{-i\vec{k}\cdot\vec{x}} \hat{\rho}(x) dx \quad .
\tag{2.18}
$$

If the interaction is weak, the inclusive cross section may be calculated in Born approximation by summing over the unobserved states $|\psi_\beta\rangle$ of the system having energy $E_\beta = E_\alpha + \omega$

$$
\sigma(q, \omega) = 2\pi \sum_\beta \delta(E_\beta - E_\alpha - \omega) \tilde{v}(q)^2 |\langle\psi_\beta|\rho(-q)|\psi_\alpha\rangle|^2 \quad .
\tag{2.19}
$$

Writing the δ-function in terms of a time integral and using completeness, this may be recast in the following form

$$
\begin{aligned}
\sigma(q, \omega) &= \tilde{v}(q)^2 \int dt e^{i\omega t} \sum_\beta \langle\psi_\alpha|e^{iE_\alpha t}\hat{\rho}(q)e^{-iE_\beta t}|\psi_\beta\rangle\langle\psi_\beta|\hat{\rho}(-q)|\psi_\alpha\rangle \\
&= \tilde{v}(q)^2 \int dt e^{i\omega t} \int dx dy e^{-iq(x-y)} \langle\psi_\alpha|e^{iHt}\hat{\rho}(x)e^{-iHt}\hat{\rho}(y)|\psi_\alpha\rangle \quad .
\end{aligned}
\tag{2.20}
$$

Summing over a complete set of states $|\psi_\alpha\rangle$ with thermal weighting factors yields the desired result that the inclusive cross section is specified by the correlation function $\langle\hat{\rho}^{(H)}(x, t)\hat{\rho}^{(H)}(y, o)\rangle$.

The inclusive cross section or structure function $\sigma(q, \omega)$ has been measured for a variety of systems of physical interest. Striking examples which will be discussed in Chapter 5 are liquid He^3 and He^4, for which the combination of neutron scattering and X-ray scattering provide high-precision results over a wide dynamical range. From Eq. (2.20), the integral $\int d\omega \sigma(q, \omega)$ yields the Fourier transform of the two-body correlation function $\langle\hat{\rho}(x)\ \hat{\rho}(y)\rangle$ which has now been measured to impressively high accuracy for liquid He. Equation (2.20) applies equally well to a finite system at zero temperature in its ground state, and extensive high-precision data are now available from inclusive electron scattering from finite nuclei.

From these considerations, we are led to the conclusion that a wide range of observables of direct experimental interest may be expressed in terms of the thermal average of products of operator at different times. This motivates the definition of Green's functions, which on one hand are the thermal averages of time-ordered products of operators that are the most convenient to calculate in perturbation theory and on

the other hand can be related by suitable analytic continuation to the quantities arising from experimental observables.

The n-body real-time Green's function is defined by

$$
\begin{aligned}
\mathcal{G}^{(n)}&(\alpha_1 t_1, \ldots \alpha_n t_n | \alpha_1' t_1', \ldots \alpha_n' t_n') \\
&= (-i)^n \langle T[a_{\alpha_1}^{(H)}(t_1) \ldots a_{\alpha_n}^{(H)}(t_n) a_{\alpha_n'}^{(H)\dagger}(t_n') \ldots a_{\alpha_1'}^{(H)\dagger}(t_1')] \rangle
\end{aligned}
\tag{2.21}
$$

where $a_\alpha^{(H)}(t)$ and $a_\alpha^{(H)\dagger}(t)$ denote annihilation and creation operators in the Heisenberg representation, Eq. (2.14). T denotes a time-ordered product, and the brackets denote a thermal average. Aside from θ-functions restricting relative times arising from the time-ordered product, all the response functions discussed above may be expressed in terms of two-particle Green's functions with suitable choice of the time arguments. We will demonstrate in Chapter 5 that when $\mathcal{G}$ is Fourier transformed from time to frequency ω, the effect of the θ function is merely to displace poles infinitesimally above or below the real axis and that physical observables may be obtained staightforwardly from Green's functions.

When one writes a real-time Green's function explicitly in terms of the thermal weighting factor $e^{-\beta(H-\mu N)}$ and Heisenberg operators $e^{iHt}a_\alpha e^{-iHt}$, the simultaneous appearance of real and imaginary times multiplying H is formally inconvenient. It is therefore advantageous to define thermal, or imaginary-time, Green's functions as follows:

$$
\begin{aligned}
\mathcal{G}^{(n)}&(\alpha_1 \tau_1, \ldots \alpha_n \tau_n | \alpha_1' \tau_1', \ldots \alpha_n' \tau_n') \\
&= \langle T[a_{\alpha_1}^{(H)}(\tau_1) \ldots a_{\alpha_n}^{(H)}(\tau_n) a_{\alpha_n'}^{(H)\dagger}(\tau_n') \ldots a_{\alpha_1'}^{(H)\dagger}(\tau_1')]
\end{aligned}
\tag{2.22}
$$

where $a_\alpha^{(H)\dagger}(\tau)$ and $a_\alpha^{(H)}(\tau)$ are the imaginary-time Heisenberg representation of $a_\alpha^\dagger$ and a_α

$$
a_\alpha^{(H)\dagger}(\tau) = e^{\tau(\hat{H}-\mu\hat{N})} a_\alpha^\dagger e^{-\tau(\hat{H}-\mu\hat{N})}
\tag{2.23a}
$$

$$
a_\alpha^{(H)}(\tau) = e^{\tau(\hat{H}-\mu\hat{N})} a_\alpha e^{-\tau(\hat{H}-\mu\hat{N})}
\tag{2.23b}
$$

and T now orders operators in imaginary time. Note that $a_\alpha^\dagger(\tau)$ and $a_\alpha(\tau)$ are not Hermitian adjoints. In Chapter 5 we will also show how real-time Green's functions can be obtained easily from imaginary-time Green's functions by analytic continuation.

The essential conclusion of this section is that the physical observables of interest may be obtained by analytic continuation of imaginary-time Green's functions. We will subsequently show in the remainder of this chapter how thermal averages of time-ordered products of Heisenberg operators in imaginary time emerge naturally from path integrals and how to evaluate them in perturbation theory.

APPROXIMATION STRATEGIES

We will presently develop a number of techniques which formally appear to provide a systematic sequence of successive approximations for many-particle systems. To maintain a realistic perspective, however, we should consider at the outset what level