A1.1 Thermodynamic relations

Following is a list of the most commonly encountered thermodynamic functions. They are expressed in terms of their natural variables. This means that if a variational parameter, such as a condensate field, is introduced, the given function is an extremum with respect to variations in the parameter with all natural variables held fixed. To obtain an intensive function from an extensive function in the large-volume, thermodynamic, limit either divide by the volume or differentiate with respect to it. Only one chemical potential is indicated; the generalization to an arbitrary number of conserved charges is obvious. For a general reference, see Landau and Lifshitz [1] and Reif [2].

Grand canonical partition function:

$$Z(\mu, T, V) = \text{Tr} \exp[-\beta(H - \mu \hat{N})]$$
(A1.1)

Thermodynamic potential density:

$$\Omega(\mu, T) = -\frac{T \ln Z}{V} = -P(\mu, T)$$

$$Vd\Omega = -SdT - PdV - Nd\mu$$

$$\frac{S}{V} = \left(\frac{\partial P}{\partial T}\right)_{\mu}$$

$$\frac{N}{V} = \left(\frac{\partial P}{\partial \mu}\right)_{T}$$
(A1.2)

Energy:

$$E = E(N, S, V)$$

$$dE = TdS - PdV + \mu dN$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

(A1.3)

Helmholtz free energy:

$$F = F(N, T, V) = E - TS$$

$$dF = -SdT + PdV + \mu dN$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

(A1.4)

Gibbs free energy:

$$G = G(N, P, T) = E - TS + PV$$

$$dG = -SdT + VdP + \mu dN$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{N,T}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

(A1.5)

A1.2 Microcanonical and canonical ensembles

The level density is defined as

$$\sigma(E) = \sum_{\text{states } s} \delta(E - E_s) \tag{A1.6}$$

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The number of states with energies between E and $E + \Delta E$ is the integral

$$\mathcal{N}(E, \Delta E) = \int_{E}^{E + \Delta E} dE' \sigma(E') \tag{A1.7}$$

This will be a choppy discontinuous function for low energies but will approach a smooth continuous function at high energies when many states are contained within the energy window ΔE . If there are conserved charges, such as baryon number or electric charge, the sum over states should be restricted to those that have the specified values. For one conserved charge with fixed value N,

$$\sigma(E,N) = \sum_{s} \delta(E - E_s) \delta_{N,N_s}$$
(A1.8)

The conserved charge involves a Kronecker rather than a Dirac delta function because charge is always discrete. Specifying the exact energy and charge numbers of a system leads to the microcanonical ensemble. This is the situation for an isolated system.

The level density can always be expressed as the Laplace transform of the grand canonical partition function. For example, for a system with no conserved charges,

$$\sigma(E) = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} d\beta \,\mathrm{e}^{\beta E} Z(\beta) \tag{A1.9}$$

where

$$Z(\beta) = \operatorname{Tr} e^{-\beta H}$$

This may be illustrated by applying it to the massless, self-interacting, scalar field theory discussed in Chapter 3. From (3.56) we know that

$$\ln Z = V\left(\frac{\pi^2}{90\beta^3}\right)c(\lambda) \tag{A1.10}$$

where

$$c(\lambda) = 1 - \frac{5}{24} \left(\frac{9\lambda}{\pi^2}\right) + \frac{5}{18} \left(\frac{9\lambda}{\pi^2}\right)^{3/2} + \cdots$$

Hence

$$\sigma(E) = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} d\beta \,\mathrm{e}^{f(\beta)} \tag{A1.11}$$

where

$$f(\beta) = \beta E + \ln Z \tag{A1.12}$$

Asymptotically, when $V \to \infty$ and $E \to \infty$ with E/V fixed, we can evaluate the level density using the saddle-point approximation. The location of the saddle point is determined by $df/d\beta = 0$. This occurs when

$$\beta^4 = \frac{\pi^2 V}{30E} c(\lambda) \tag{A1.13}$$

(It is legitimate to neglect the β -dependence of λ induced by the renormalization group to the order $\lambda^{3/2}$ at that we are working.) Then

$$\sigma(E) \approx \left[\frac{\mathrm{e}^{f}}{\sqrt{2\pi d^{2} f/d\beta^{2}}}\right]_{\mathrm{saddle \ point}}$$
$$= aV^{1/8}E^{-5/8}\exp\left(bV^{1/4}E^{3/4}\right)$$
(A1.14)

where

$$a = \frac{1}{2} \left(\frac{c(\lambda)}{480\pi^2} \right)^{1/8} \quad b = \frac{4}{3} \left(\frac{\pi^2 c(\lambda)}{30} \right)^{1/4}$$
(A1.15)

The saddle point value of β is therefore just the inverse temperature. Notice that the saddle point condition (A1.13) can also be written as

$$\frac{E}{V} = \frac{\pi^2}{30} T^4 c(\lambda) \tag{A1.16}$$

that agrees with the energy density obtained via -P + TdP/dT from (3.56). Furthermore, the level density (A1.14) agrees with that derived on the basis of single-particle phase space [3] when we set $\lambda = 0$.

The canonical ensemble refers to a system in a box of volume V, maintained at temperature T by thermal contact with a heat reservoir but with a fixed number of conserved charges. For a system with just one conserved charge, say baryon number, the canonical partition function is

$$Z_{\rm c}(N,T,V) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \,\mathrm{e}^{-i\theta N} Z(\theta) \tag{A1.17}$$

where

$$Z(\theta) = \operatorname{Tr} e^{-\beta H + i\theta \hat{N}}$$

Notice the integral representation of the Kronecker delta on account of the discreteness of baryon number. Make the change of variable $\theta = -i\beta\mu$. Then

$$Z = \operatorname{Tr} e^{-\beta(H-\mu\hat{N})}$$
(A1.18)

that is the familiar form, albeit with an imaginary chemical potential.

As an illustration, recall the partition function for a massless noninteracting gas of fermions:

$$\ln Z = \frac{V}{12\pi^2\beta^3} \left(\beta^4 \mu^4 + 2\pi^2\beta^2 \mu^2 + \frac{7}{15}\pi^4 \right)$$
(A1.19)

Then

$$Z_{\rm c} = \frac{\beta}{2\pi i} \int d\mu \, \mathrm{e}^{f(\mu)} \tag{A1.20}$$

where

 $f = -\beta \mu N + \ln Z$

The saddle point is determined by the condition

$$\frac{N}{V} = \frac{\mu}{3\pi^2} \left(\mu^2 + \pi^2 T^2\right)$$
(A1.21)

which is just the expression for the baryon density in the grand canonical ensemble, namely, $\partial P(\mu, T)/\partial \mu$. In the large-volume limit with fixed intensive quantities,

$$Z_{\rm c}(N,T,V) \approx V^{-1/2} \left(\frac{2T\mu^2}{\pi} + \frac{2\pi T^3}{3}\right)^{-1/2} \\ \times \exp\left[\frac{V}{12\pi^2} \left(-\frac{3\mu^4}{T} - 2\pi^2 T\mu^2 + \frac{7\pi^4 T^3}{15}\right)\right] \quad (A1.22)$$

In this equation, μ is given by (A1.21) as a function of N/V and T. Up to corrections of relative order $(\ln V)/V$ the canonical partition function is

$$T \ln Z_{\rm c} = T \ln Z - \mu N = PV - \mu N = -F$$
 (A1.23)

It is also possible to fix the total three-momentum of the system [4] and to pick out the singlet states of SU(N) gauge theories [5]. Different boundary conditions on the surface, such as periodic, Dirichlet, Neumann, and Cauchy, result in contributions to the free energies that scale as the surface area but with differing coefficients. Compared with the volume contributions they are of no importance in the large-volume, thermodynamic, limit and so we do not discuss them further.

A1.3 High-temperature expansions

Frequently a high-temperature $(T \gg m)$ expansion of an integral like

$$h_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{dx \ x^{n-1}}{\sqrt{x^2 + y^2}} \frac{1}{e^{\sqrt{x^2 + y^2}} - 1}$$
(A1.24)

is desired, where y = m/T. These integrals satisfy the differential equation

$$\frac{dh_{n+1}}{dy} = -\frac{yh_{n-1}}{n} \tag{A1.25}$$

The high-temperature expansion is obtained by using the identity

$$\frac{1}{\mathrm{e}^z - 1} = \frac{1}{z} - \frac{1}{2} + 2\sum_{l=1}^{\infty} \frac{z}{z^2 + (2\pi l)^2}$$
(A1.26)

multiplying the integrand by $x^{-\epsilon}$, integrating term by term, and letting $\epsilon \to 0$ at the end. One obtains

$$h_1(y) = \frac{\pi}{2y} + \frac{1}{2}\ln\left(\frac{y}{4\pi}\right) + \frac{1}{2}\gamma_{\rm E} - \frac{1}{4}\zeta(3)\left(\frac{y}{2\pi}\right)^2 + \frac{3}{16}\zeta(5)\left(\frac{y}{2\pi}\right)^4 + \cdots$$
(A1.27)

where $\gamma_{\rm E} = 0.5772 \dots$ is Euler's constant and $\zeta(3) = 1.202 \dots$, $\zeta(5) = 1.037 \dots$ are specific values of the Riemann zeta function $\zeta(n)$. Also

$$h_2(y) = -\ln(1 - e^{-y})$$
 (A1.28)

For example, the pressure of a noninteracting spinless boson field is

$$P = \frac{4T^4}{\pi^2} h_5\left(\frac{m}{T}\right) = \frac{\pi^2}{90} T^4 - \frac{m^2 T^2}{24} + \frac{m^3 T}{12\pi} - \frac{m^4}{32\pi^2} \left[\ln\left(\frac{4\pi T}{m}\right) - \gamma_{\rm E} + \frac{3}{4}\right] + \mathcal{O}\left(\frac{m^6}{T^2}\right) \quad (A1.29)$$

The analysis for a noninteracting charged spinless boson field is only slightly more complicated. See Haber and Weldon [6] for details. In the limit $T \gg m > |\mu|$ the pressure is

$$P = \frac{\pi^2}{45}T^4 - \frac{(m^2 - 2\mu^2)T^2}{12} + \frac{(m^2 - \mu^2)^{3/2}T}{6\pi} + \frac{(3m^2 - \mu^2)\mu^2}{24\pi^2} - \frac{m^4}{16\pi^2} \left[\ln\left(\frac{4\pi T}{m}\right) - \gamma_{\rm E} + \frac{3}{4} \right] + \mathcal{O}\left(\frac{m^6}{T^2}, \frac{m^4\mu^2}{T^2}\right) A1.30$$

For fermions with zero chemical potential the integral of interest is

$$f_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{dx \ x^{n-1}}{\sqrt{x^2 + y^2}} \frac{1}{e^{\sqrt{x^2 + y^2}} + 1}$$
(A1.31)

The f_n satisfy the same differential equation as the h_n ,

$$\frac{df_{n+1}}{dy} = -\frac{yf_{n-1}}{n}$$
(A1.32)

To evaluate the fermion integral, insert the factor $x^{-\epsilon}$, integrate term by term using the expansion

$$\frac{1}{e^z + 1} = \frac{1}{2} - \sum_{l=-\infty}^{\infty} \frac{z}{z^2 + (2l+1)^2 \pi^2}$$
(A1.33)

and let $\epsilon \to 0$ at the end. One obtains [7]

$$f_1(y) = -\frac{1}{2} \ln\left(\frac{y}{\pi}\right) - \frac{1}{2}\gamma_{\rm E} + \cdots$$

$$f_2(y) = \ln(1 + e^{-y})$$
(A1.34)

For a noninteracting gas of fermions with $\mu = 0$ the pressure is

$$P = \frac{16T^4}{\pi^2} f_5\left(\frac{m}{T}\right) = \frac{7\pi^2}{180} T^4 - \frac{m^2 T^2}{12} + \frac{m^4}{8\pi^2} \left[\ln\left(\frac{\pi T}{m}\right) - \gamma_{\rm E} + \frac{3}{4}\right] + \mathcal{O}\left(\frac{m^6}{T^2}\right) (A1.35)$$

Notice the absence of an m^3T term, that is present for bosons. For small mass and small chemical potential the high-temperature expansion begins as

$$P = \frac{7\pi^2}{180}T^4 + \frac{(2\mu^2 - m^2)T^2}{12} + \dots$$
 (A1.36)

A1.4 Expansion in the degeneracy

The pressure of a noninteracting gas may be expressed as

$$P = (2s+1)T \int \frac{d^3p}{(2\pi)^3} \ln\left(1 \pm e^{-\beta(\omega-\mu)}\right)^{\pm 1}$$
(A1.37)

Here s is the spin, while the upper sign refers to fermions and the lower sign to bosons. The logarithm may be expanded in powers of the exponential and then integrated term by term:

$$P = \frac{(2s+1)m^2T^2}{2\pi^2} \sum_{l=1}^{\infty} \frac{(\mp)^{l+1}}{l^2} e^{l\mu\beta} K_2(lm\beta)$$
(A1.38)

Here K_2 is a modified Bessel function of the second kind. This is an expansion in powers of the quantum degeneracy.

The number density, entropy density, and energy density may be calculated using the thermodynamic identities:

$$n = \frac{(2s+1)m^2T}{2\pi^2} \sum_{l=1}^{\infty} \frac{(\mp)^{l+1}}{l} e^{l\beta\mu} K_2(l\beta m)$$

$$s = \frac{(2s+1)m^2T^2}{2\pi^2} \sum_{l=1}^{\infty} \frac{(\mp)^{l+1}}{l^2} e^{l\beta\mu} \Big[(2-l\beta\mu) K_2(l\beta m) + \frac{1}{2}\beta m \left(K_1(l\beta m) + K_3(l\beta m) \right) \Big]$$

$$\epsilon = \frac{(2s+1)m^3T}{2\pi^2} \sum_{l=1}^{\infty} \frac{(\mp)^{l+1}}{l} e^{l\beta\mu} \Big[K_1(l\beta m) + \frac{3}{l\beta m} K_3(l\beta m) \Big] \quad (A1.39)$$

These expressions do not include contributions from the antiparticles, if they exist; they may be obtained by the substitution $\mu \to -\mu$. The nonrelativistic limit may be obtained by using the expansions of the Bessel functions $K_n(x)$ when $x \gg 1$:

$$K_n(x) = \sqrt{\frac{\pi}{2x}} e^{-x} \left[1 + \frac{4n^2 - 1}{8x} + \frac{(4n^2 - 1)(4n^2 - 9)}{2!(8x)^2} + \cdots \right]$$
(A1.40)

Numerical approximations for both bosons and fermions have been worked out for arbitrary values of m, T, μ by Johns, Ellis, and Lattimer [8].

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