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Chemical potential: Gibbs-Duhem approach

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The most commonly used method of calculating the chemical potential in quantum statistical mechanics is based on an idea originally due to Sommerfeld, applicable to a Fermi system. An alternative approach is presented that relies on the extensivity property of the energy on an isentrope. A simple equivalence is demonstrated through the ideal gas models given in the polylogarithm formulation. Unlike the Sommerfeld approach this approach is also applicable to a Bose system. [S1063-651X(96)10305-6]

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I. INTRODUCTION

In modern statistical mechanics the chemical potential μ is a fundamental quantity characterizing many-particle systems in thermal equilibrium [1]. For the ideal Fermi gas in the ground state, the chemical potential is the same as the Fermi energy. For a semiconductor or an insulator it lies halfway in a gap between the valence and conduction bands. For the ideal Bose gas the vanishing of the chemical potential signals the onset of Bose condensation. For a thermal photon gas the chemical potential is zero since the numbers are not conserved. That is, these photons are in a state of coexistence at all temperatures. For liquid ^{4}He at $T=0$ K, the chemical potential is the same as the ground state binding energy (-7.16 K), which is equal in magnitude to the latent heat of vaporization.

From the second law of thermodynamics $dU=TdS-PdV+\mu dN$ (the symbols have the usual meaning), one obtains at once $\mu_{\mathrm{GD}}=(\partial U/\partial N)_{S,V}$, where we have inserted the subscript GD for Gibbs-Duhem for reasons that will become apparent shortly. Thus the chemical potential is a measure of the extensivity property of the energy on an isentrope when the volume V is also fixed. This particular constraint makes the determination of the chemical potential from the energy nontrivial except perhaps in the ground state where the entropy is zero. If a system is not in the ground state, one needs to separately determine an isentropic path on which the energy varies with the number of particles N (or with the density if the volume is fixed). The sign on the chemical potential is a consequence of this constraint imposed by the second law. We shall term it the Gibbs-Duhem approach when the chemical potential is obtained in this manner on an isentrope.

In the Gibbs-Duhem approach we are already thinking of a system whose volume is fixed but number is not. It is just the condition on which a grand ensemble is constructed in statistical mechanics. In grand ensemble theory the density (more accurately the reduced density) is expressible as a function of the fugacity $z=\exp\beta\mu$, where $\beta=1/kT$, k the Boltzmann constant. Thus by inversion the fugacity or the chemical potential is obtainable. One might term this process of obtaining the chemical potential the Sommerfeld approach, most widely used in quantum statistical mechanics of Fermi particles [1]. In the Sommerfeld approach one is in effect on an isotherm. Hence, it is thermodynamically very different from the Gibbs-Duhem approach.

The purpose of this paper is to show that the Gibbs-Duhem approach, although seldom used in quantum statistical mechanics, can yield the chemical potential nearly as directly for the ideal Fermi system as the Sommerfeld approach. It is perhaps more insightful thermodynamically as it utilizes almost all the main statistical thermodynamics results obtained by grand ensemble theory. In addition, the Gibbs-Duhem approach can directly yield the chemical potential for the ideal Bose system, also near the transition temperature. Standard ways of obtaining it are somewhat indirect, requiring an artificial function [6]. The Sommerfeld approach, of course, ceases to be applicable for a Bose system at low temperatures.

II. STATISTICAL THERMODYNAMICS OF IDEAL PARTICLES AND POLYLOGARITHMS

It was shown recently that the statistical thermodynamics of ideal particles given by grand ensemble theory is simply unifiable [2]. If $\rho\equiv N/V$ is the number density of an ideal gas in d dimensions and λ the thermal wavelength, then the reduced density is expressible as follows:

$$\rho\lambda^d=\mathrm{sgn}(\zeta)Li_{d/2}(\zeta),\qquad \zeta=\begin{cases} z & \text{if Bose} \\ -z & \text{if Fermi,}\end{cases} \tag{1}$$

where $z=\exp\beta\mu$ is the fugacity and $Li_{d/2}(\zeta)$ is the polylog of order $d/2$. The physically allowed domain ranges from $\zeta=-\infty$ to 1, whereupon the polylog is also real. A useful integral representation of the polylog of order $m+1$ in s is [2]

$$Li_{m+1}(s)=\frac{1}{\Gamma(m+1)}\int_0^s(\alpha-\ln t)^m\frac{dt}{1-t},\qquad \alpha=\ln s, \tag{2}$$

where s may be a complex number.

From (2) one can deduce a recurrence relation $s d/ds\, Li_{m+1}(s)=Li_m(s)$ as well as asymptotic forms $Li_m(s\to 0)=s$ and $Li_m(s\to-\infty)=-(\ln -s)^m/\Gamma(m+1)$.

All the important thermodynamic functions can be expressed in polylogs through their relationship to the density. For example,

$$\beta^{-1}\rho P=Li_{d/2+1}(\zeta)/Li_{d/2}(\zeta)\equiv f_1(\zeta), \tag{3}$$

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$$\beta U/N=(d/2)f_1(\zeta), \tag{4}$$

$$S/Nk=(d/2+1)f_1(\zeta)-\ln|\zeta|. \tag{5}$$

The above (3)–(5) stand as unified expressions of these thermodynamic functions at any T, d, and statistics. Their existence is critical to the applicability of the Gibbs-Duhem approach.

III. GIBBS-DUHEM APPROACH

Since the volume is held constant throughout, it will not be indicated explicitly henceforth. We shall show by (3)–(5) that whether the statistics is Fermi, Bose, or classical,

$$\mu_{\mathrm{GD}}\equiv\partial(U/V)/\partial\rho|_S=\mu, \tag{6}$$

where by the right-hand side of (6) we shall mean the chemical potential obtained by the Sommerfeld approach. Although possible to do so generally, it is simpler—perhaps more revealing—to show it separately according to the statistics. In the Gibbs-Duhem approach there are two isentropic relationships A and B, through which the chemical potential is expressed. They are defined below:

$$A=\partial\ \ln\beta/\partial\ \ln\rho|_S, \tag{7a}$$

$$B=\partial\ \ln z/\partial\ \ln\rho|_S, \tag{7b}$$

which evidently depend on ζ through (1) and (5), hence on the statistics.

The classical gas is given by the condition $\zeta\rightarrow\pm0$, hence $Li_{d/2}(\zeta)=\zeta$. See after (2). That is, the polylog acts self-similarly, which explains why the classical properties are generally d independent. If $Li_{d/2}(\zeta)=\zeta$, $f_1(\zeta)=1$. Hence from (4), we obtain

$$\mu_{\mathrm{GD}}=(d/2)\beta^{-1}(1-A). \tag{8}$$

From the reduced density (1),

$$1+(d/2)A=B. \tag{9}$$

From the entropy (5),

$$B=d/2+1-\ln z. \tag{10}$$

Hence, by (9) and (10),

$$\mu_{\mathrm{GD}}=\beta^{-1}\ln z=\beta^{-1}\ln\rho\lambda^d, \tag{11}$$

where for the final step we have used (1). We recognize the above at once as the classical result. In the classical regime, $A\sim B\rightarrow-\ln z$, $z\rightarrow0$.

For the classical gas, if (1) and (4) are combined,

$$U/N=(d/2)a\rho^{2/d}e^{-(d/2)\ln z}, \tag{12}$$

where a is defined by $\lambda=(a\beta)^{1/2}$. Now by (5),

$$U/N=(d/2)a\rho^{2/d}e^{d/2\{S/Nk-(d/2+1)\}}. \tag{13}$$

The above is exactly the energy obtained by microcanonical ensemble theory after resolving the Gibbs paradox of mixing. See p. 27 of Ref. [1]. Now the chemical potential can also be directly obtained by differentiation on an isentrope, which was perhaps the original way of calculating it. At low temperatures it is of course not possible to express the energy in the form of (13) since the energy depends on the entropy very weakly if at all.

Now let us turn to the Fermi gas near the ground state, i.e., $z\rightarrow\infty$. If $z\rightarrow\infty$, there is an asymptotic expression for the polylog. See also (2). Hence we obtain

$$U/V=\frac{\rho\beta^{-1}\ln z}{1+2/d}+\cdots\ . \tag{14}$$

To this order, by (6),

$$\mu_{\mathrm{GD}}=\frac{\beta^{-1}\ln z}{1+2/d}\{1-A+B/\ln z\}. \tag{15}$$

Now from (1), replacing the polylog therein with its asymptotic form, we obtain

$$1+(d/2)A=(d/2)B/\ln z, \tag{16}$$

which may be compared with the classical relation (9).

By substituting (16) in (15), we finally obtain

$$\mu_{\mathrm{GD}}=\beta^{-1}\ln z \tag{17a}$$

$$\begin{aligned}&=-\beta^{-1}Li_{d/2}{}^{-1}(-\rho\lambda^d)\\&=\beta^{-1}[\Gamma(d/2+1)\rho\lambda^d]^{2/d}+\cdots\ ,\end{aligned} \tag{17b}$$

where we have introduced the inverse polylog. If $d=3$, (17b) is precisely the result first given by Sommerfeld [1], and later more generally by others [3–5]. From the entropy (5), we obtain $B=\ln z$, $z\rightarrow\infty$, hence by (16) $A=1-2/d$. A is a constant while B is divergent in the ground state, different from the classical behavior, where A and B are both divergent as $-\ln z$, $z\rightarrow0$.

Finally we shall turn to the ideal Bose gas, for which the Gibbs-Duhem approach is especially useful. Recall that the Sommerfeld approach is not applicable here. Most interesting is the behavior near $z=1$, where the polylog has a branch point, depending sensitively on its order, i.e., the dimensionality d [2]. It is thus necessary to begin the analysis exactly. By (4) and (6),

$$\mu_{\mathrm{GD}}=(d/2)\beta^{-1}f_1[1-A+(f_1{}^{-1}-f_0{}^{-1})B], \tag{18}$$

where $f_0=Li_{d/2}(\zeta)/Li_{d/2-1}(\zeta)$ and f_1 defined in (3). In deriving this we have used $\partial f_1/\partial\zeta=\zeta^{-1}(1-f_1/f_0)$, obtained by the aid of the recurrence relation. See after (2). Now from the reduced density (1),

$$1+(d/2)A=f_0{}^{-1}B. \tag{19}$$

Also from the entropy (5),

$$f_0{}^{-1}B=\frac{\ln z-(d/2+1)f_1}{(d/2+1)(f_0-f_1)-f_0}. \tag{20}$$

The substitution of (19) and (20) in (18) directly yields the desired identity

$$\mu_{\mathrm{GD}}=\beta^{-1}\ln z. \tag{21}$$

If $z \rightarrow 1$, the polylog of order $d/2$ has a finite value if $d=3,5,\ldots$ [2]. That is,

$$Li_{d/2}(z \rightarrow 1) \simeq \Gamma(-d/2+1)(-\ln z)^{d/2-1} + Z(d/2), \quad (22)$$

where $Z(d/2)$ is the Riemann zeta function, i.e., $Li_{d/2}(z=1)=Z(d/2)=\rho\lambda_c^d$ by (1). Hence, if $z \rightarrow 1$,

$$\ln z = -[(\rho\lambda^d - \rho\lambda_c^d)/\Gamma(-d/2+1)]^{2/(d-2)}. \quad (23)$$

By substituting (23) in (21), we obtain the chemical potential as $\lambda \rightarrow \lambda_c$ (i.e., $T \rightarrow T_c$)

$$\mu_{\mathrm{GD}} = -\beta^{-1}\left[\frac{Z(d/2)}{\Gamma(-d/2+1)}[1-(\lambda/\lambda_c)^d]\right]^{2/(d-2)}, \quad \lambda \leqslant \lambda_c. \quad (24)$$

If $d=3$, we recover the known result, but obtained somewhat indirectly [6]. Both A and B vanish as $-(-\ln z)^{1/2}$, $z \rightarrow 1$.

If $d=1$ or 2, the polylog is divergent as $z \rightarrow 1$, i.e.,

$$Li_{1/2}(z \rightarrow 1) \sim \Gamma(1/2)(-\ln z)^{-1/2}, \quad (25)$$

$$Li_1(z \rightarrow 1) \sim -\ln(-\ln z). \quad (26)$$

Hence there are no finite critical temperatures in these dimensions, as is well known [1]. Finally the expression (21) being exact may be used to recover the previous results (11) and (15) by taking the $z \rightarrow 0$ and ∞ limits in the polylog, respectively.

IV. DISCUSSION

We have shown that for a Fermi system the Gibbs-Duhem approach yields the chemical potential quite equivalently to the more commonly used Sommerfeld approach. For a Bose system the Gibbs-Duhem approach also yields the chemical potential readily. Since this approach refers to the extensivity property of the energy on an isentrope, it can give added insight into thermodynamic behavior through the two quantities $A=\partial \ln\beta/\partial \ln\rho|_S$ and $B=\partial \ln z/\partial \ln\rho|_S$. The dependence of the chemical potential on statistics or temperature, or even the sign itself, is determined by how A and B both behave in different regions of the fugacity. For the Fermi gas near its ground state, A is a constant but B diverges as $z \rightarrow \infty$. For the Bose gas near the transition temperature, both A and B vanish as $z \rightarrow 1$ if $d=3$. In the classical regime, they instead diverge as $z \rightarrow 0$.

Independent of the chemical potential, the isentropic behavior of thermodynamic quantities, such as the temperature and fugacity, is itself interesting, especially compared with the isothermal behavior. Finally, as an aside, we have shown that the classical energy obtained in a grand ensemble can be put into a well-known form given by microcanonical ensemble theory. One cannot expect the same at low temperatures where a microcanonical ensemble would prove inadequate.

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