Review

FERMIONIC CHEMICAL POTENTIAL

M. Howard LEE

Department of Physics and Astronomy, University of Georgia, Athens, GA 30602, USA

Abstract

This paper gives a critical review of the physical meaning of the chemical potential, perhaps the most abstract of all thermodynamic quantities. To show its basic behavior, thereby to illustrate its physical significance, we have derived the chemical potential of a system of free electrons as a function of the density and temperature in different spatial dimensions. We have shown how to obtain the isothermal compressibility given the chemical potential. To emphasize the usefulness of the knowledge of dimensional dependence, both the compressibility and average kinetic energy are expressed as simple dimensional relationships of the density and, hence, the chemical potential. Finally, there is a certain temperature at which the chemical potential should identically vanish. Physical implications of zero chemical potential are discussed.

1.   Introduction

The chemical potential μ is an important thermodynamic potential expressing a physical state of a large system. It is a thermodynamic variable conjugate to N, the number of particles in a system. One of its standard definitions is: $\mu = (\partial U/\partial N)_{S,V}$, where U, S, and V are, respectively, energy, entropy and volume of a system. It states that the chemical potential is the energy necessary to add one particle to a system without changing both the entropy and volume. It is also a useful quantity. The isothermal compressibility may be obtained from it. One of the necessary conditions for phase or chemical equilibria is provided by the chemical potential [1].

In spite of its importance and usefulness, the chemical potential remains an abstract thermodynamic quantity. It is neither absolutely positive nor negative. Its sign, in fact, can depend on temperature and particle statistics. In addition, it is not directly calculable via the formalism of statistical mechanics. It must ordinarily be obtained from other quantities, e.g. the density. Its absolute significance is unmasked only at the lowest possible temperature. At very low temperatures, the chemical potential shows dimensional dependence including an even–odd effect [2]. As the temperature rises, the dependence on the dimensions begins to disappear. These are a few examples of the subtler properties of the chemical potential.

Recognizing its relevance to the thermodynamics of metals, we shall consider a system of N free electrons homogeneously distributed over a volume of D dimensions. At the lowest temperature $(T = 0)$, these electrons, following the Pauli principle, uniformly fill single-particle energy eigenstates starting from the lowest level to a maximum level referred to as the Fermi energy ε_F. This constitutes the ground state of our system of N free electrons. If one were to add one more free electron to this ground state without changing the volume, the minimum necessary energy is thus the Fermi energy. Since the entropy of these electrons in the N-particle ground state is zero, adding an electron in the lowest available level above the Fermi energy does not affect the entropy. Hence, the chemical potential at $T = 0$ is just the Fermi energy and the chemical potential at $T = 0$ is a positive energy quantity.

As the temperature rises, the distribution of these filled states changes since some electrons near the Fermi energy can take up higher energy states, vacating the states they had previously occupied. This change in the distribution of occupied states results in a change in the chemical potential. What is the chemical potential now? Is it greater or less than at $T = 0$? It turns out that it is greater in one dimension but less in two and three dimensions.

Sommerfeld [3] first showed how to calculate the chemical potential of N free electrons in three dimensions at finite T. His calculation is somewhat crude but physically intuitive. Recently, Barker [4] has shown a more elegant way using an idea due to Blankenbecler [5]. This work can be generalized to all dimensions [6]. In this review article, each of these calculations will be explained in some detail. It is hoped that these explicit calculations will help to make the chemical potential seem less abstract.

In recent years, there has been much interest in the physics and chemistry of low dimensions, stimulated by device fabrication. Also, high dimensions are regarded as a domain where mean-field theories become valid. These modern developments have freed us from three dimensions. In fact, they have encouraged us to look at physical properties in other dimensions, where one occasionally finds surprises in store.

2. Statistical basis of chemical potential

Let N be the number of particles in a volume $V = L^D$, where D denotes the dimensionality and L the length. Let $n(k)$ be the momentum distribution of states of particles such that

$$N = \sum_k n(k). \tag{1}$$

On physical grounds, one may assume $n(k)$ to be non-negative for any value of the momentum k. If these particles are electrons, the momentum distribution *per spin state* is a function of the chemical potential and momenta. It is given as

$$n(\boldsymbol{k}, z) = (1 + z^{-1}\exp\beta\varepsilon)^{-1}, \tag{2}$$

where $z = \exp\alpha$, $\alpha = \beta\mu$, $\beta = 1/kT$, $\varepsilon = \boldsymbol{k}^2/2m$; m is the mass of the electron [1].

In the thermodynamic limit (i.e. $N, V \to \infty$, but $\rho \equiv N/V \to$ const.) one can replace the sum over $\boldsymbol{k}$ in (1) with an integral. For an isotropic system, one obtains the density per spin state

$$\rho = h^{-D}\int d^D\boldsymbol{k}\, n(\boldsymbol{k}, z) = h^{-D}\upsilon_D \int_0^\infty dk\, k^{D-1} n(\boldsymbol{k}, z), \tag{3}$$

where $\upsilon_D = 2\pi^{D/2}/\Gamma(D/2)$, and h is the Planck constant. Changing the variable from k to $\varepsilon = \boldsymbol{k}^2/2m$, we can express the density per spin more conveniently as

$$\rho = \tfrac{1}{2}\left(2m/h^2\right)^{D/2}\upsilon_D \int_0^\infty d\varepsilon\, \varepsilon^{-1+D/2} n(\varepsilon, z). \tag{4}$$

The chemical potential μ is contained in the integrand of the above equation through $n(\varepsilon, z)$. Thus, it must be obtained from the fugacity z, which must be extracted from the expression for the density. The resulting chemical potential will be found to be a function of the temperature T, and density ρ, and dimensionality D. One should, therefore, note that the dependence of the chemical potential on these parameters is derived, and not intrinsic.

3. Chemical potential at high temperature

If the temperature is high (i.e. $\beta \to 0$), the distribution function $n(\varepsilon, z)$ may be expanded as follows:

$$n(\varepsilon, z) = \frac{1}{1 + z^{-1}\exp\beta\varepsilon} = \sum_{n=1}^\infty (-1)^{n+1}z^n\exp(-n\beta\varepsilon). \tag{5}$$

Substituting (5) into (4), one can carry the integration term-by-term and obtain

$$\rho\lambda^D = \sum_{n=1}^\infty (-1)^{n+1}z^n n^{-D/2} \equiv K_{D/2}(z), \tag{6}$$

where $\lambda = (2\pi m\, kT/h^2)^{-1/2}$ is the thermal de Broglie wavelength. By a reversion process, we obtain

$$\alpha = \beta\mu = \log(\rho\lambda^D) + a(\rho\lambda^D) + b(\rho\lambda^D)^2 + \dots, \tag{7}$$

where $a = 2^{-D/2}$, $b = 3 \times 2^{-D-1} - 3^{-D/2}$, etc. Since $\rho\lambda^D \to 0$ at $T \to \infty$, the log term in (7) is dominant. We recover the well-known classical expression

$$\mu = kT \log (\rho\lambda^D). \tag{7a}$$

In the classical regime, the subtle dependence of the chemical potential on the dimensions expressed through the coefficients a, b, etc., becomes completely lost in the presence of the dominant log term. Since $\rho\lambda^D < 1$ in this regime, the chemical potential is negative. Hence, the fugacity is bounded by $0 < z < 1$. The expansion (6) is thus convergent.

Now, if $T \to 0$, $\rho\lambda^D \to 1$. Thus, the log term is no longer important and the power series terms may not be neglected. In this regime, in fact, $z > 1$. Hence, the expansion (6) is not convergent. One must look for another way to obtain the chemical potential.

There is, however, one special solution of interest that can be obtained from (6). Let $D = 2$ in (6). Then, we obtain immediately

$$\rho\lambda^2 = \log(1 + z). \tag{8}$$

Hence,

$$z = \exp\beta\mu = -1 + \exp(\rho\lambda^2). \tag{9}$$

This solution is valid for any temperature. If $T \to 0$, one obtains

$$\mu = \rho h^2/2\pi m + O(T). \tag{9a}$$

The leading term is a positive quantity, independent of the temperature. This is just the energy required to add one particle to the system at $T = 0$, holding the entropy and volume fixed. We shall later show that (8) can also be obtained from a low temperature formulation.

4. Low temperature chemical potential in odd-numbered dimensions

4.1. METHOD OF SOMMERFELD

We shall now consider (4) at low temperatures, At $T = 0$, we observe from (2) that $n(\varepsilon, z) = 1$ if $0 \leq \varepsilon \leq \mu_0$; $n(\varepsilon, z) = 0$ if $\varepsilon > \mu_0$, where by μ_0 we mean the chemical potential at $T = 0$. That $n(\varepsilon, z)$ is non-negative implies that μ_0 is also non-negative. Hence, by definition, μ_0 must be the Fermi energy ε_F, the highest occupied single-particle energy in constituting the ground state of a system of N free electrons. Then, one obtains from (4) that

$$\rho = (2\pi m\, \mu_0/h^2)^{D/2}\, \Gamma(1 + D/2) \tag{10a}$$

or

$$\rho\lambda^D = \alpha_0^{D/2}\, \Gamma(1 + D/2), \tag{10b}$$

where Γ is the gamma function and $\alpha_0 = \beta\mu_0$. Observe that when $D = 2$, it is a result already obtained in (9a).

Eliminating the density in favor of the zero-temperature chemical potential μ_0, we can rewrite (4) in the following dimensionless form:

$$\alpha_0^{D/2} = (D/2)\, I(\alpha), \tag{11}$$

where

$$I(\alpha) = \int_0^\infty dx\, x^{-1 + D/2} n(x, \alpha), \tag{11a}$$

with $\alpha = \beta\mu$. Note that $I(\alpha_0) = (2/D)\, \alpha_0^{D/2}$.

Looking at (11), one might expect that $I(\alpha)$ would behave analytically in the vicinity of $T = 0$. This turns out to be true if D is an odd number. Although Sommerfeld [3] considered it when $D = 3$ only, it is not much more difficult to study (11) for the entire family of odd-numbered dimensions, as we shall do here. This will show us the dimensional relationship in the chemical potential at low temperatures, which will be found useful.

Observe in the integrand of (11a) that if $x \to \infty$, $n(x, \alpha) \to \exp -(x - \alpha)$. Hence, main contributions come from the range of x for which $n(x, \alpha)$ is not exponentially damped. This behavior becomes more apparent if we look at the derivative of $n(x, \alpha) = n(x - \alpha, 0) \equiv n(x - \alpha)$. Then,

$$d/dx\, n(x - \alpha) = \frac{-1}{(1 + \exp(x - \alpha))(1 + \exp -(x - \alpha))} \equiv -g(x - \alpha). \tag{12}$$

This function $g(x - \alpha)$ is symmetric about $x = \alpha$ and it is peaked at $x = \alpha$. At $T = 0$, it is in fact a delta function. As T increases, the peak spreads out smoothly.

To use the above-noted properties, one needs merely to convert $n(x - \alpha)$ to $g(x - \alpha)$ by writing $x^{-1 + D/2} = (2/D)\, d/dx\, x^{D/2}$. Hence, it is convenient to define $f_D(x) = x^{D/2}$. Then

$$(D/2)\, I(\alpha) = \int_0^\infty dx\, f_D(x)\, g(x - \alpha). \tag{13}$$

Hence, from (11),

$$\alpha_0^{D/2} = \int_{-\alpha}^\infty dx\, f_D(\alpha + x)\, g(x). \tag{14}$$

If $T \to 0$, $\alpha \to \infty$. Since $g(x)$ is now peaked at its origin ($x = 0$), one might extend the lower limit from $-\alpha$ to $-\infty$ without affecting the value of the integral (14). The error of this approximation is of the order of $\exp - \alpha$ (see appendix A). If $f_D(x + \alpha)$ is an infinite series – as it is when D is an odd number – then the error is small and negligible. However, if $f_D(x + \alpha)$ is an entire function (e.g. a polynomial) – as it is when D is an even number – the error is still small but now not negligible. For this reason, the method of Sommerfeld may be used only when D is an odd integer number.

Let D be an odd integer number. We next Taylor-expand $f_D(\alpha + x)$ about $x = 0$ where $g(x)$ is peaked, and then carry out term-by-term integration. We obtain

$$\alpha_0^{D/2} = \sum_{n=0}^{\infty} h_{2n}(\alpha)\bar{g}_{2n}/(2n!), \tag{15}$$

where

$$h_n(\alpha) = (d/d\alpha)^n f_D(\alpha) \tag{16}$$

and

$$\bar{g}_n = \int_{-\infty}^{\infty} dx\, x^n g(x). \tag{17}$$

Both h_n and $\bar{g}_n$ may be readily evaluated. Thus,

$$(\alpha_0/\alpha)^{D/2} = 1 + (\pi^2/6.2^2)D(D - 2)\, \alpha^{-2}$$
$$+ (7\pi^4/360.2^4)D(D - 4)\, \alpha^{-4} + \dots . \tag{18}$$

By reverting the above expression, we obtain

$$\alpha/\alpha_0 = 1 - (\pi^2/2.3!)(D - 2)\, \alpha_0^{-2}$$
$$- (\pi^4/2.6!)(D - 2)(D - 6)(D - 9)\, \alpha_0^{-4} - \dots . \tag{19}$$

Observe the appearance of $(D - 2)$ in the coefficients of expansion. Because of the presence of this factor, the chemical potential in $D = 1$ is distinguished from that in all other odd-numbered dimensions. If $D = 1$, the chemical potential initially increases with the temperature. In all other odd-numbered dimensions, the chemical potential decreases with the temperature. That is, it takes more energy to add a particle at $T > 0$ than at $T = 0$ if $D = 1$. It takes less energy if $D = 3, 5, \dots$. Below, we give a few examples:

$$\alpha/\alpha_0 = 1 + (\pi^2/12)\, \alpha_0^{-2} + (\pi^4/36)\, \alpha_0^{-4} + \dots \qquad (D = 1).$$
$$\alpha/\alpha_0 = 1 - (\pi^2/12)\, \alpha_0^{-2} - (\pi^4/80)\, \alpha_0^{-4} - \dots \qquad (D = 3).$$
$$\alpha/\alpha_0 = 1 - (\pi^2/4)\, \alpha_0^{-2} - (\pi^4/120)\, \alpha_0^{-4} - \dots \qquad (D = 5).$$

For odd-numbered dimensions, the chemical potential is an analytic function of the temperature T and it is regular at $T = 0$. Our results show a definite dimensional dependence in the chemical potential at low temperatures, absent at high temperatures. This kind of dimensional dependence has its origin in quantum mechanics.

4.2.   THE METHOD OF BARKER

Now returning to (14), we shall write it out explicitly:

$$\alpha_0^{D/2} = \int_0^\infty dx \, (\alpha + x)^{D/2} e^x (1 + e^x)^{-2}. \tag{20}$$

Blankenbecler [5] notes that one can write

$$f_D(\alpha + x) \equiv (\alpha + x)^{D/2} = e^{x\delta} \alpha^{D/2} = e^{x\delta} f_D(\alpha) \tag{21}$$

as a series where $\delta = \partial/\partial\alpha$. Next, let $s = e^x$. Then, (20) may be expressed as [4]

$$\alpha_0^{D/2} = \int_{z^{-1}}^\infty ds \, \frac{e^{x\delta}}{(1+s)^2} f_D(\alpha), \tag{22}$$

where $z^{-1} = \exp(-\alpha)$. As $T \to 0$, $z^{-1} \to 0$. Hence, as in the method of Sommerfeld, we may replace the lower limit by zero, provided that the error is negligible (see appendix A). As already noted, the error is negligible if D is an odd number.

The above integral may be evaluated by a contour integration as follows: Consider a closed contour c, shown in fig. 1. Regarding s as a complex number, we may write

$$\frac{1}{2\pi i} \int_c ds \, \frac{s^\delta}{(1+s)^2} = \text{(residue at } s = -1). \tag{23}$$

Referring to the contour shown in fig. 1, we draw a branch line on the positive real axis from $s = 0$ to $s = \infty$. Contributions from the small and great circles clearly vanish. Hence,

$$\int_c ds \, \frac{s^\delta}{(1+s)^2} = \int_\infty^0 ds \, \frac{(s e^{2\pi i})^\delta}{(1+s)^2} + \int_0^\infty ds \, \frac{s^\delta}{(1+s)^2}. \tag{24}$$

The residue of a second-order pole at $s = -1$ is $\delta \exp(i\pi(\delta - 1)) = -\delta\exp(i\pi\delta)$. Therefore,

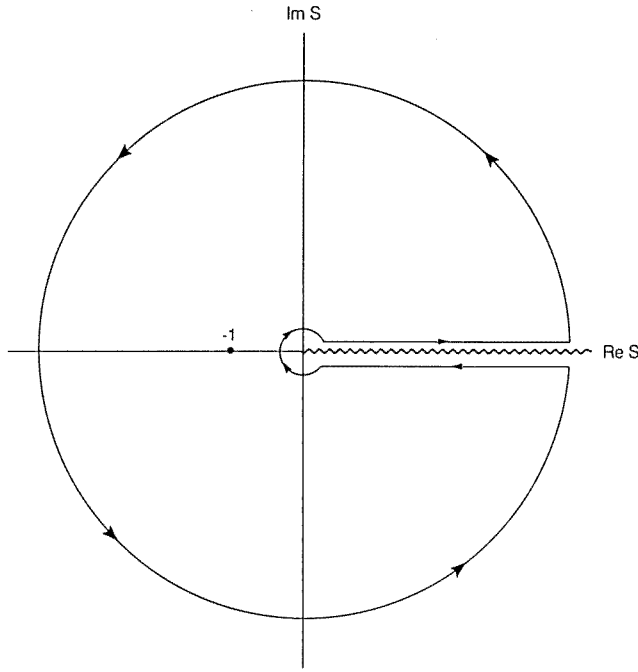$$\int_0^\infty ds \, \frac{s^\delta}{(1+s)^2} = \pi\delta/\sin\pi\delta. \tag{25}$$

Fig. 1. The contour of integration shown in eq. (25) (after Barker, see ref. [4]). The arrows indicate the directions of integration. The radius of the small circle is arbitrarily small, while the radius of the great circle is arbitrarily large. Also indicated is one simple pole at $s = \exp i\pi$, encircled by the path of integration.

Hence, we obtain a very simple looking formal result for (22):

$$\alpha_0^{D/2} = (\pi\delta/\sin\pi\delta)f_D(\alpha). \tag{26}$$

One may interpret the operator standing before $f_D(\alpha)$ as follows:

$$\pi\delta/\sin\pi\delta = 1 + (1/6)(\pi\delta)^2 + (7/360)(\pi\delta)^4 + \dots . \tag{27}$$

By applying repeatedly the differential operator $\delta = \partial/\partial\alpha$ on $f_D(\alpha)$ as required, one can evaluate the right-hand side of (26). One then recovers the results already given in (18).

One can obtain the above result perhaps most simply if one changes the variable in (22) to $s = y/(1-y)$ [6,7]. Then, the integral may be put in a standard form of the beta function [8]:

$$\int_0^\infty ds \frac{s^\delta}{(1+s)^2} = \int_0^\infty dy\, y^\delta(1-y)^{-\delta} = B(1+\delta, 1-\delta)$$

$$= \Gamma(1+\delta)\Gamma(1-\delta)/\Gamma(2) = \pi\delta/\sin\pi\delta. \tag{28}$$

5. Low temperature chemical potential in even-numbered dimensions

When D is an even number, the methods of Sommerfeld and Barker lead to an inaccurate solution for the chemical potential. This inaccuracy points out an interesting property when an analytic function is also an entire function (e.g. a polynomial). In the method of Sommerfeld, also of Barker, the lower limit of an integral expression of the chemical potential is made to go to $-\infty$. This approximation introduces an error of the order of $\exp(-\alpha)$, as shown in appendix A. This error is evidently smaller than any positive integer power of $(1/\alpha)$ as $\alpha \to \infty$. Although small, whether this error is negligible depends on a certain analytic property of the function $f_D(\alpha)$.

If $f_D(\alpha)$ is analytic in some domain (i.e. $\alpha^{-1} < 1$), then the chemical potential may be expressed as

$$\alpha_0^{D/2} = \alpha^{D/2} \sum_{m=0}^{M} c_{2m} \alpha^{-2m}, \tag{29}$$

where c_m's are numerical coefficients depending on D. If D is not an even number, $M \to \infty$, where M is the upper limit of the sum (29). Thus, the error introduced by the above-mentioned approximation is no larger than the smallest term of the above expansion, α^{-2M} as $M \to \infty$. Hence, the approximation is entirely justified (i.e. the error is negligible). If D is an even number, $f_D(\alpha)$ is an entire function of α. Hence, now $M < \infty$. The approximation is no longer negligible.

When D is an even number, it is thus necessary to evaluate the chemical potential from the exact expression (11) [6]

$$\alpha_0^k = k \int_{-\alpha}^{\infty} dx \frac{(\alpha + x)^{k-1}}{1 + e^x}, \tag{30}$$

where $k \equiv D/2 = 1, 2, 3, \dots$. It does not appear possible to obtain a general solution from (30). Hence, we shall consider it for some special values of D.

(1) *D = 2*

From (30), it follows directly that

$$\alpha_0 = \int_{-\alpha}^{\infty} dx \frac{1}{1 + e^x} = \int_{-z^{-1}}^{\infty} dy \left(\frac{1}{y} - \frac{1}{y+1} \right) = \ln(1 + z), \tag{31}$$

where $z = \exp \alpha$. Hence,

$$e^{\alpha_0} = 1 + e^{\alpha}, \tag{32}$$

which is also the expression obtained from the high temperature series expansion. This exact solution (32) for $D = 2$ turns out to be the only closed form expression possible for any D, even or odd. It is useful for testing, for example, approximations.

For low temperatures, we obtain the following expansion:

$$\alpha_0 = \alpha + e^{-\alpha} - (1/2)e^{-2\alpha} + (1/3)e^{-3\alpha} - \dots \,. \tag{33}$$

If the method of Sommerfeld or Barker were applied, one would have obtained only the leading term of the r.h.s. of (33), thereby missing all the correction terms. It would indeed be a poor approximation. Note also that each of the correction terms is equal to or smaller than $\exp(-\alpha)$.

At low temperatures, $\alpha \approx \alpha_0$. Hence, α is a positive number since α_0 is a positive number. However, at high temperatures it follows from (32) that α (hence μ) must be negative, since $\alpha_0 \approx 0$. This implies that at a certain temperature, say T^*, the sign of the chemical potential μ changes. That is, $\mu(T^*) = 0$. This point will be further discussed in section 7.

(2) $D = 4$

From (30) we have

$$\alpha_0^2 = 2(\ln z)(\ln(1+z)) + 2 \int_{-\alpha}^{\infty} dx \, \frac{x}{1+e^x}, \tag{34}$$

where $z = \exp\alpha$.

The integral on the r.h.s. of (34) cannot be expressed in terms of elementary functions, but it can be given a series expansion as follows:

$$2 \int_{-\alpha}^{\infty} \frac{dx\, x}{1+e^x} = (\ln(1+z^{-1}))^2 - (\ln z)^2 + 2h(z^{-1}), \tag{35}$$

where

$$h(z^{-1}) = \sum_{n=1}^{\infty} n^{-2}(1+z^{-1})^{-n}. \tag{36}$$

Substituting (35) into (34), we obtain

$$\alpha_0^2 = (\ln(1+z))^2 + 2h(z^{-1}). \tag{37}$$

For $z^{-1} \to 0$, one may replace $h(z^{-1})$ by $h(0) = \pi^2/6$, i.e.

$$(\ln(1+z))^2 \approx \alpha_0^2 - \pi^2/3. \tag{38}$$

Hence, one may write approximately:

$$e^{\alpha} = -1 + e^{\alpha_0}(1 - (\pi^2/6\alpha_0) + \dots). \tag{39}$$

If one were to neglect $h(z^{-1})$, then (37) is exactly the same as the solution for $D = 2$ (see eq. (32)). For higher even-numbered dimensions, one can obtain the chemical potential in essentially the same way. It will have a structure shown in (39). From the solutions for $D = 2$ and 4, it is quite clear that the low-temperature behavior of the chemical potential in even-numbered dimensions is very different from that in odd-numbered dimensions. Also, unlike in odd-numbered dimensions, $T = 0$ behaves like an essential singular point.

Finally, using (6) and (10a), we can write

$$\alpha_0^k = \Gamma(k + 1) \sum_{n=1}^{\infty} (-1)^{n+1} z^n n^{-k}, \tag{40}$$

where $k = D/2$. One may immediately verify that (37) corresponds to (40) if $D = 4$.

6. Chemical potential and compressibility

One very useful role of the chemical potential is played by its connection to the isothermal compressibility or susceptibility χ_T, defined as [1]

$$\chi_T = \rho^{-2}(\partial\rho/\partial\mu)_{T,V}. \tag{41}$$

Since T is held fixed, one may also write (41) as:

$$\tilde{\chi}_T \equiv (\rho/\beta)\chi_T = (1/\rho\lambda^D)\partial/\partial\alpha(\rho\lambda^D) = (1/\rho\lambda^D)z\partial/\partial z(\rho\lambda^D), \tag{42}$$

where $z = \exp\alpha$. If T is high such that $z < 1$, then from (6) it follows that

$$\tilde{\chi}_T(D) = K_{D/2-1}(z)/K_{D/2}(z) \tag{43a}$$

$$= \rho(D-2)\lambda^{D-2}/\rho(D)\lambda^D, \tag{43b}$$

where we have inserted D to indicate the relevant dimensions. In obtaining (43), we have used the property that for any number p,

$$z\, d/dz\, K_p(z) = K_{p-1}(z), \tag{44}$$

where

$$K_p(z) = \sum_{n=1}^{\infty} (-1)^{n+1} z^n / n^p. \tag{45}$$

Although (43b) is derived for $z < 1$ (high temperature), one can also prove that it is valid for $z > 1$ (low temperature). This is shown in appendix B.

If $D = 2$, our analytic solution (8) provides a ready application. Noting that for $D = 2$, $\rho\lambda^2 = \alpha_0$ (see (10b)), we obtain from (42) in (43a) that the susceptibility per spin is given by

$$\tilde{\chi}_T(D = 2) = \frac{z}{(1 + z)\log(1 + z)} = \frac{z}{(1 + z)\alpha_0}. \tag{46}$$

The compressibility is finite for all non-negative values of z. If $T \to \infty$, $\chi_T \to \beta/\rho$, which is the classical limit. If $T \to 0$, $\chi_T \to 1/(\rho\mu_0)$, which is the quantum limit. Observe that the susceptibility (46) is maximum at $T = 0$ and it smoothly vanishes with T. Also, (43b) and (46) imply that $\rho(D = 0) = z/(1 + z) \to 1$ with (10b), i.e. $z \to \infty$ in $D = 0$. That is, in zero dimension (if meaningful) there is no classical regime!

For odd-numbered dimensions at low temperatures, we can use (18) in (43b) to obtain the susceptibility per spin at once,

$$\chi_T(D) = (D/2\rho\mu_0)(1 + a_D\alpha^{-2} + O(\alpha^{-4})), \tag{47}$$

where $a_D = -(\pi^2/6)(D - 2)$, etc.

If $D \geq 3$, a_D is negative. Hence, the susceptibility decreases with T. If $D = 1$, then the susceptibility increases with T. This behavior is quite similar to the behavior of the chemical potential itself. At $T = 0$, the susceptibility is finite.

For the high temperature susceptibility, we obtain using (43a)

$$\chi_T(D) = (\beta/\rho)(1 - 2^{D/2-1}z + O(z^2)), \tag{48}$$

which is valid in any dimension, even or odd. We recognize the well-known classical limit.

7.   Concluding remarks

The chemical potential, as noted, is an abstract thermodynamic quantity. In an effort to make it more familiar, we have calculated the chemical potential of free electrons. In particular, we have shown some of the subtler properties, such as its dependence on the temperature and dimensions. There is one additional point of some interest, to which we shall now turn our attention.

At high temperatures the chemical potential is negative, but at lower temperatures its sign changes. Hence, at a certain temperature, say $T = T^*$, the chemical potential

must have zero value. It is not difficult to calculate T^*. For $D = 2$, we use our analytic solution (32) to obtain: $\mu_0/kT^* = \ln 2 = 0.69314\ldots$. For $D > 2$, one can obtain T^* from a general relation using (6) and (10b):

$$\Gamma(1 + D/2)(\mu_0/kT^*)^{D/2} = (1 - 2^{1-D/2})\zeta(D/2),\qquad(49)$$

where $\zeta(D/2)$ is the Riemann-zeta function [8]. One can see that this temperature is such that (μ_0/kT^*) is of order unity (i.e. macroscopic).

We shall now examine the physical significance of this temperature T^*. From thermodynamics, we know $\mu = (-\partial S/\partial N)_{U,V}$. At $T = T^*$, $\mu = 0$ by definition. Then, the entropy S must become independent of the number N, hence, the density ρ. That is, the number states are indefinite at this temperature. Such an unusual physical state, i.e. $\mu = 0$ at a finite T, also exists in a system of free Bose particles in $D = 3$. An examination of the same phenomenon in a Bose system may be helpful even though the two systems are generally quite dissimilar.

If $T > T_{BE}$, where T_{BE} means the Bose–Einstein condensation temperature, there is one homogeneous phase of Bose particles with an N-dependent entropy. The chemical potential is negative. As $T \to T_{BE}$ from above, $\mu \to 0$. At $T = T_{BE}$, there appears a new phase (Bose condensed phase) with zero entropy and zero chemical potential. This new phase is thus in equilibrium with the original (uncondensed) phase. The uncondensed phase has an entropy, but it is now N-independent. That is, the number states are indefinite. Even as $T \to 0$, the chemical potential of each phase still remains zero. Hence, both phases remain in equilibrium. However, more and more particles enter the condensed phase from the uncondensed phase without affecting their entropies. Thus, there is a range of temperatures $(0 < T < T_{BE})$ in which the two phases can and do coexist with zero chemical potential. As a result, the isothermal susceptibility is divergent throughout.

Now let us return to our system of free electrons. The chemical potential of this system, unlike that of a Bose system, can be both positive and negative. Let the state of a positive chemical potential be referred to as a quantum phase and the state of a negative chemical potential as a classical phase. The two phases (not like the two Bose phases) can never be in equilibrium except at one unique point $T = T^*$ when $\mu = 0$. The susceptibility is thus finite (as in a low-dimensional Bose system for which $T_{BE} = 0$).

In grand ensemble theory in statistical mechanics [1], the chemical potential provides a weighting factor for number states through $\exp(\mu N/kT)$, just as the temperature does for energy states through $\exp(-U/kT)$ in canonical ensemble theory. In the classical phase of electrons, small number states are thus favored, whereas in the quantum phase, large number states are favored. At $T \to T^*$ from above, more and more of larger number states begin to be counted. At $T = T^*$, all number states are equally probable. As T falls below T^*, the system now flops over into the quantum phase. One may thus regard T^* as either the lowest limit of the classical regime or the highest limit of the quantum regime of free electrons.

Appendix A

Error bound

In the methods of Sommerfeld and Barker, there is an approximation intro-duced at the outset. The lower limit of a certain integral (see (14)) is extended from $-\alpha$ to $-\infty$ as shown below:

$$\int_{-\alpha}^{\infty} dx\, f_D(\alpha + x) g(x) \rightarrow \int_{-\infty}^{\infty} dx\, f_D(\alpha + x) g(x), \tag{A1}$$

where f_D and $g(x)$ are already defined (see eq. (12) and following) and $\alpha > 0$. Usually, this approximation is taken to be sufficiently accurate since the function $g(x)$ is peaked at its origin. Below, we shall give an estimate of errors introduced by this approxi-mation.

Consider the following:

$$I_k = \int_{-\infty}^{-\alpha} dx\, \frac{|\alpha + x|^k\, e^x}{(1 + e^x)^2} = \int_{\alpha}^{\infty} dx\, \frac{|\alpha - x|^k\, e^{-x}}{(1 + e^{-x})^2}, \tag{A2}$$

where $k = D/2$. This quantity is the difference between the exact and approximate expressions given in (A1) except for an absolute sign. An absoulte sign is introduced to simplify our argument, which cannot affect the order of magnitude in this problem. It then follows that

$$I_k \leq \int_{\alpha}^{\infty} dx\, |\alpha - x|^k\, e^{-x} = \Gamma(k + 1) e^{-\alpha}. \tag{A3}$$

Therefore, we may conclude that errors due to the approximation (A1) are of the order of $e^{-\alpha}$, which is smaller than any positive integer power of $(1/\alpha)$ as $\alpha \rightarrow \infty$.

Appendix B

Susceptibility and density

Using (10b) and (30), we can express the D-dimensional density as

$$\rho(D) \lambda^D = \frac{1}{\Gamma(D/2)} \int_{-\alpha}^{\infty} dx\, \frac{(\alpha + x)^{-1 + D/2}}{1 + e^x}. \tag{B1}$$

Now differentiate both sides with respect to α, holding T and V fixed:

$$\mathrm{d}/\mathrm{d}\,\alpha(\rho(D)\lambda^D) = \frac{1}{\Gamma(D/2-1)}\int_{-\alpha}^{\infty}\mathrm{d}x\,\frac{(\alpha+x)^{-2+D/2}}{1+e^x} = \rho(D-2)\lambda^{D-2},\quad D>2. \quad (B2)$$

Using the definition of the reduced susceptibility $\tilde{\chi}_T(D)$ (see (42)), we obtain: If $D>2$,

$$\tilde{\chi}_T(D) = (1/\rho(D)\lambda^D)\partial/\partial\alpha(\rho(D)\lambda^D) = \rho(D-2)\lambda^{D-2}/\rho(D)\lambda^D. \quad \square \quad (B3)$$

Result (B3) attaches an interesting physical interpretation to the reduced isothermal susceptibility. The susceptibility in D dimensions represents a certain relationship of the density in dimensions $D-2$ and D. This is one reason why the knowledge of dimensional dependence is useful. Because of this relationship, the susceptibility in an even-numbered dimension is related to that in other even-numbered dimensions. A similar relationship exists between odd-numbered dimensions, but not between even- and odd-numbered dimensions (sometimes referred to as an even–odd effect). There is a similar effect to be found in a system of free Bose particles.

Appendix C

Density and average kinetic energy

In appendix B we have shown that if $D>2$, the isothermal susceptibility $\chi_T(D)$ may be expressed as a relationship of the density in dimensions $D-2$ to dimensions D. One can show that a similar relationship exists in the average kinetic energy.

Let the density in dimensions D be written as (see eq. (4)):

$$\rho(D)\lambda^D = \frac{1}{\Gamma(D/2)}\int_0^{\infty}\mathrm{d}x\,G(x,z;D), \quad (C1)$$

where

$$G(x,z;D) = x^{-1+D/2}n(x,z), \quad (C2)$$

with $n(x,z)$ given by (2). The average kinetic energy per particle may be defined as

$$\langle\varepsilon\rangle = \sum_k n(k)\,\varepsilon/\sum_k n(k). \quad (C3)$$

Converting the sum into an integral, we may write

$$\sum_k n(k)\varepsilon \rightarrow \frac{1}{\beta\lambda^D\Gamma(D/2)}\int_0^{\infty}\mathrm{d}x\,x\,G(x,z;D) \quad (C4a)$$

$$= (D\lambda^2/2\beta)\rho(D+2). \quad (C4b)$$

In obtaining (C4b), we have used the relation

$$xG(x, z; D) = G(x, z; D + 2). \tag{C5}$$

Hence,

$$\beta\langle\varepsilon\rangle = (D/2)\,\lambda^2\rho(D+2)/\rho(D), \tag{C6a}$$

or

$$\langle\varepsilon\rangle = (h^2/2\pi m)\,\rho(D+2)/\rho(D). \tag{C6b}$$

That is, the average kinetic energy is a relationship of the density in dimensions $D + 2$ to dimensions D. It is in the opposite direction to the relationship found for the isothermal susceptibility. It implies that the susceptibility can be more singular than the energy.

At low temperatures, using (18) we obtain

$$\langle\varepsilon\rangle/\mu_0 = (D/D+2)(1 + (\pi^2/12)(D+2)\,\alpha_0^{-2} + \ldots). \tag{C8}$$

Observe that at $T = 0$ and $D = 3$, we recover the well-known result that $\langle\varepsilon\rangle = (3/5)\mu_0$.

At high temperatures, using (6) we obtain

$$\beta\langle\varepsilon\rangle = (D/2)(1 + (1/2)^{D/2+1} z + \ldots). \tag{C9}$$

We also recognize the limiting high temperature solution at once.

Acknowledgements

References

[1] R.K. Pathria, *Statistical Mechanics* (Pergamon, Oxford, 1972).
[2] N.L. Sharma and M.H. Lee, J. Math. Phys. 27(1986)1618;
     M.H. Lee and J.T. Nelson, J. Math. Phys. 31(1990)686.
[3] A. Sommerfeld, Z. Phys. 47(1928)1.
[4] W.A. Barker, J. Math. Phys. 27(1986)302; 28(1987)1385, 1389.
[5] R. Blankenbecler, Amer. J. Phys. 25(1957)279.
[6] M.H. Lee, J. Math. Phys. 30(1989)1837.
[7] C. Kittel, *Elementary Statistical Mechanics*(Wiley, New York, 1958), p. 93. See also
     C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, New York, 1980), p. 192.
[8] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*, Natl. Bur. Stds., Appl. Math.
     Ser. No. 55 (US GPO, Washington, DC, 1970), p. 258.