IEEE Open Journal of Nanotechnology

Received 27 November 2022; accepted 1 January 2023. Date of publication 10 January 2023;
date of current version 10 February 2023. The review of this article was arranged by Associate Editor Masahiro Nomura.

Digital Object Identifier 10.1109/OJNANO.2023.3234042

Dirac Materials and an Identity for the Grand Potential of the Nondegenerate Statistical Thermodynamic Regime

NORMAN J. M. HORING

Department of Physics, Stevens Institute of Technology, Hoboken, NJ 07030 USA

ABSTRACT We examine the question "Can Dirac materials exist in a nondegenerate statistical state?," deriving and employing an identity for the thermodynamic Grand Potential Ω (per unit volume/area) in the low density nondegenerate statistical regime, relating it to the density n as $\Omega = -\beta^{-1}n$ ($\beta^{-1} = \kappa_B T$ is thermal energy, κ_B is the Boltzmann constant, and T is Kelvin temperature). The implications of this identity for Dirac materials are explored. The identity is universally valid for all thermodynamic systems in equilibrium in the nondegenerate, low density statistical regime, irrespective of size, dimensionality or applied static fields. Phenomena that may contribute to the realization of such a nondegenerate statistical equilibrium state in Dirac materials are discussed.

INDEX TERMS Dirac materials, nondegenerate statistical identity, grand potential, statistical state of nondegeneracy.

I. GRAND POTENTIAL FOR NONDEGENERATE SYSTEMS

The nondegenerate statistical regime is characterized by the Maxwell-Boltzmann statistical distribution function, ie: the exponentially decreasing "tail" of the temperature dependent Fermi-Dirac distribution, $f(\epsilon_i) = \frac{1}{1+e^{\beta(\epsilon_i-\mu)}}$ (μ is the chemical potential, ϵ_i are the eigenenergies). As such, the Maxwell-Boltzmann distribution is related to the Fermi-Dirac distribution by a low density approximation involving $e^{\beta(\epsilon_i-\mu)} \gg 1$ (alternatively, $e^{-\beta(\epsilon_i-\mu)} \ll 1$), for *all* ϵ_i; and it may be accessed as the leading term of the fugacity ($e^{\mu\beta}$) expansion of the Fermi-Dirac distribution, specifically

$$f^{(\mathrm{nd})}(\epsilon_i) \cong e^{-\beta(\epsilon_i-\mu)} \equiv e^{\mu\beta}e^{-\beta\epsilon_i}, \tag{1}$$

where the superscript "(nd)" denotes nondegeneracy.

The grand potential, Ω, is defined by (F is the Helmholtz Free Energy, Z is the Grand Partition Function, and N is number) [1], [2], [3], [4]

$$\Omega = F - \mu N = -\beta^{-1}\ln Z, \tag{2}$$

and for Fermions it takes the form

$$\begin{aligned}\Omega &= -\beta^{-1}\sum_{\epsilon_i}\ln\left(1+e^{\beta(\mu-\epsilon_i)}\right)\\ &= -\beta^{-1}\sum_{\epsilon_i}\ln\left(1+e^{-\beta(\epsilon_i-\mu)}\right).\end{aligned} \tag{3}$$

The leading term of Ω in the low density fugacity expansion is given by

$$\begin{aligned}\Omega^{(\mathrm{nd})} &\cong -\beta^{-1}\sum_{\epsilon_i}e^{-\beta(\epsilon_i-\mu)}\\ &= -\beta^{-1}e^{\beta\mu}\sum_{\epsilon_i}e^{-\beta\epsilon_i}\\ &\to -\beta^{-1}e^{\beta\mu}\sum_{\epsilon_i}e^{-\beta\epsilon_i}D(\epsilon_i).\end{aligned} \tag{4}$$

The ϵ_i energy state summations in (1–4) above are extended over the entire spectrum of energy eigenstates, including their degeneracies as indicated on the right of (4) by the explicit appearance of $D(\epsilon_i)$ as the density of states (which will be understood implicitly below). In this same level of approximation described by the leading term of the fugacity expansion

for low density, the equilibrium density n,

$$n = \sum_{\epsilon_i} f(\epsilon_i) = \sum_{\epsilon_i} \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}}, \tag{5}$$

is approximately given by

$$n^{(\mathrm{nd})} \cong \sum_{\epsilon_i} e^{-\beta(\epsilon_i - \mu)} = e^{\mu\beta} \sum_{\epsilon_i} e^{-\beta\epsilon_i}. \tag{6}$$

Employing this result in (4), we have the result (on a per-unit-volume/area basis)

$$\Omega^{(\mathrm{nd})} \equiv -\beta^{-1} n^{(\mathrm{nd})}, \tag{7}$$

which is a useful and universally valid thermodynamic identity of the nondegenerate statistical regime describing low density systems in equilibrium, irrespective of size, dimensionality, and static fields (albeit not well known). It should be noted that if the Dirac energy spectrum actually extended to $\epsilon_i \to -\infty$ (for any value of μ), then the condition that $e^{-\beta(\epsilon_i - \mu)} << 1$ would be violated for large negative ϵ_i and, correspondingly, the Dirac materials could not exist in the nondegenerate statistical state. However, reality sets in with the recognition that Dirac materials are understood to be limited to the low energy regime, and we explore the conditions for their existence in the nondegenerate statistical regime in this context.

II. DIRAC MATERIALS

The "Dirac materials" include Graphene [5], [6], [7], [8], Silicene [9], Group VI Dichalcogenides [10], Topological Insulators [11], the T-3 Dice Lattice [12] and some others [13], [14]. The defining feature of Dirac materials is based on the fact that their energy spectra (and Hamiltonians) mimic those of relativistic electron/positron dynamics and are linear in momentum in the low energy regime, with both positive and negative energy branches. Of course, this description is of limited validity in that the energy bands of a crystalline solid eventually bend away from linearity. Accordingly, there is an upper limit on the positive branch of the energy spectrum ($E_{\max}$) and also a lower limit on the negative branch of the spectrum ($-E_{\min}$). This applies to both discrete Dirac spectra (eg: in the case of a normal static magnetic field inducing Landau quantization on a planar sheet of Graphene or of the Group VI Dichalcogenides) as well as applying to continuous spectra (in which case our energy sums $\sum_{\epsilon_i}$ must be understood as integrals). Denoting the restricted sum over the "relativistic" Dirac energy range

$$-E_{\min} \le \epsilon_i \le E_{\max} \quad \text{as} \quad \sum_{\epsilon_i} \to \sum_{\epsilon_i}{}', \tag{8}$$

the principal statistical thermodynamic functions of Dirac materials in the low density nondegenerate statistical regime may be summarized as follows (per unit area):

Grand Potential:

$$\Omega^{(\mathrm{nd})} = -\beta^{-1} n^{(\mathrm{nd})} = -\beta^{-1} e^{\beta\mu} \sum_{\epsilon_i}{}' e^{-\beta\epsilon_i} D(\epsilon_i); \tag{9}$$

Entropy:

$$S^{(\mathrm{nd})} = -\left(\frac{\partial \Omega^{(\mathrm{nd})}}{\partial T}\right)_{\mu} = \kappa_B \beta^2 \left(\frac{\partial \Omega^{(\mathrm{nd})}}{\partial \beta}\right)_{\mu}, \tag{10a}$$

$$S^{(\mathrm{nd})} = \kappa_B \sum_{\epsilon_i}{}' (1 - \beta[\mu - \epsilon_i])\, e^{\beta(\mu - \epsilon_i)} D(\epsilon_i); \tag{10b}$$

Specific Heat (constant volume):

$$C_V^{(\mathrm{nd})} = T\left(\frac{\partial S^{(\mathrm{nd})}}{\partial T}\right)_V = -\beta\left(\frac{\partial S^{(\mathrm{nd})}}{\partial \beta}\right)_V, \tag{11a}$$

$$C_V^{(\mathrm{nd})} = \kappa_B \sum_{\epsilon_i}{}' \beta^2 (\mu - \epsilon_i)^2 e^{\beta(\mu - \epsilon_i)} D(\epsilon_i); \tag{11b}$$

Magnetic Moment:

$$M^{(\mathrm{nd})} = -\left(\frac{\partial \Omega^{(\mathrm{nd})}}{\partial B}\right)_T = \beta^{-1}\left(\frac{\partial n^{(\mathrm{nd})}}{\partial B}\right)_{\beta}, \tag{12a}$$

$$M^{(\mathrm{nd})} = \sum_{\epsilon_i}{}' e^{\beta(\mu - \epsilon_i)} \left(-\frac{\partial \epsilon_i}{\partial B} D(\epsilon_i) + \beta^{-1} \frac{\partial D(\epsilon_i)}{\partial B}\right), \tag{12b}$$

where B is magnetic field strength.

Again, $D(\epsilon_i)$ represents the density of states of the Dirac material under consideration and ϵ_i represents its eigenenergy spectrum. $D(\epsilon_i)$ may be obtained from the trace of the imaginary part of its retarded Green's function $G_{\mathrm{ret}}(\vec{r}, \vec{r'}; \omega)$ in frequency representation as [15]

$$D(\omega) = -\frac{1}{\pi} \mathrm{Tr} \int d\vec{r}\, Im\, G_{\mathrm{ret}}(\vec{r}, \vec{r}; \omega), \tag{13}$$

and ϵ_i may be identified from its frequency poles $\omega \to \epsilon_i (\hbar \to 1)$. The pertinent Dirac Green's functions for Landau quantized Graphene [16], Group VI Dichalcogenides [17] and the Dice Lattice [18] in a magnetic field are available in the literature.

For example, the nondegenerate statistical thermodynamic functions for the Landau-quantized Group VI Dichalcogenides in a constant, uniform magnetic field B follow as (per unit area; $\gamma \cong 10^6 \frac{m}{s}$; $1_\nu \equiv \nu = +1, -1$ for K, K' valley index)

$$\textit{Grand Potential: } \Omega^{(\mathrm{nd})} = -\beta e^{\mu\beta} \frac{eB}{4\pi} \sum_{\epsilon_i}{}' R_i e^{-\beta\epsilon_i}; \tag{14}$$

$$\text{where the sum } \sum_{\epsilon_i}{}' \equiv \sum_{s_z=\pm 1} \sum_{\nu=\pm 1} \sum_{\pm} \sum_{\pm'} \sum_{n \ge 0}{}' \tag{15}$$

involves sums over spin index $s_z = \pm 1$ and valley index $\nu = \pm 1$; and the sum over the trace contributions $\pm$ arises from diagonal elements of the Green's function; also the $\pm'$ sum is over positive and negative branches of the Landau-quantized energy spectrum; and, finally, the sum over Landau level index n is limited as discussed above in this section. Also [17], for the Landau-quantized Group VI Dichalcogenides, we have

$$\epsilon_i = E_{s_z} \pm' \sqrt{g^2 + \epsilon_{n\pm}^2}; \quad \epsilon_{n\pm}^2 = (2n + 1 \mp 1_\nu)\gamma^2 eB;$$

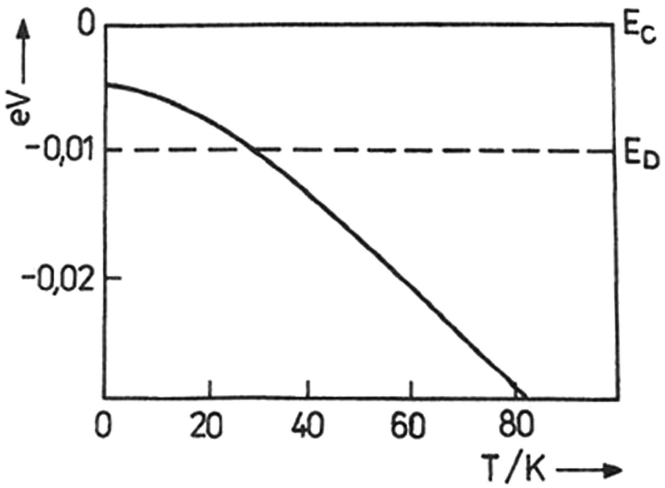

FIGURE 1. Carrier concentration of *n*-type Si as a function of temperature for $N_D = 10^{15} cm^{-3}$. *(After Smith, 1979)* By courtesy of the World Scientific Publishing Company [19].

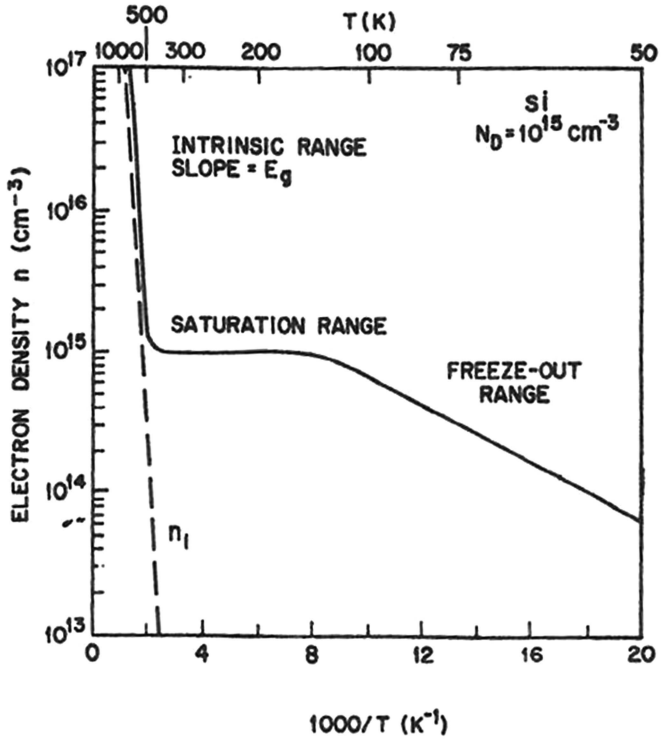

FIGURE 2. Temperature dependence of the Fermi level for *n*-type Ge assuming typical values of E_B (10*meV*) and N_D ($10^{16} cm^{-3}$). *(After Bonch-Bruevich and Kalashnikov, 1982)* By courtesy of the World Scientific Publishing Company [19].

$$R_i = \left(1 \pm \frac{(\mp' 1)g}{\sqrt{g^2 + \epsilon_{n\pm}^2}}\right), \quad (16)$$

and

$$E_{s_z} = \frac{s_z \nu \lambda}{2}; \quad g = \frac{\Delta}{2} - E_{s_z}, \quad (17)$$

with E_{s_z} representing an energy shift and λ is spin splitting and Δ is the energy gap without spin splitting. (The corresponding results for Graphene may be obtained by setting $g = 0$ and $E_{s_z} = 0$.) Furthermore, direct calculation for the Group VI Dichalcogenides yields the nondegenerate results:

Entropy:

$$S^{(\mathrm{nd})} = \kappa_B e^{\mu\beta} \frac{eB}{4\pi} {\sum_{\epsilon_i}}' R_i e^{-\beta\epsilon_i} \left(1 - \beta\left[\mu - \epsilon_i\right]\right); \quad (18)$$

Specific Heat (constant volume):

$$C_V^{(\mathrm{nd})} = \kappa_B \frac{eB}{4\pi} {\sum_{\epsilon_i}}' R_i e^{\beta(\mu-\epsilon_i)} \beta^2 (\mu - \epsilon_i)^2; \quad (19)$$

Magnetic Moment:

$$M^{(\mathrm{nd})} = \beta^{-1} \frac{e}{4\pi} e^{\mu\beta} {\sum_{\epsilon_i}}' e^{-\beta\epsilon_i} \times \left\{ R_i \left(1 \mp' \frac{\beta\epsilon_{n\pm}^2}{(g^2 + \epsilon_{n\pm}^2)^{\frac{1}{2}}}\right) \mp \frac{(\pm' 1) g \epsilon_{n\pm}^2}{2(g^2 + \epsilon_{n\pm}^2)^{\frac{3}{2}}} \right\}. \quad (20)$$

Upon inspection, this result for the magnetic moment M of the Group VI Dichalcogenides in the nondegenerate statistical regime is seen to be positive (note that $R_i > 0$), reflecting paramagnetism.

III. NONDEGENERACY AND DIRAC MATERIALS

In regard to electronic device operation of the Dirac materials in contact with another material (for example, a substrate), it should be borne in mind that the chemical potential μ is subject to change by contact with that material: If the native chemical potential of the Dirac material differs from that of the other contact material, there will be a nonequilibrium flow of charged particles between the two until a new equilibrium is established with a new chemical potential common to both [19]. With this in view the condition for prevalence of the nondegenerate statistical state may be written as

$$e^{\beta(\mu-\epsilon_i)} < 1 \quad (21)$$

for *all* of the Dirac material eigenstates ϵ_i, as discussed in Section 1, both negative and positive. Otherwise, at least some of these states will not be occupied in accordance with nondegenerate statistics. This requires that for all ϵ_i in the range defined by (8),

$$\mu - \epsilon_i < 0, \text{ in particular } \mu + E_{\min} < 0, \quad (22)$$

which is a challenge for Dirac materials since even if it is satisfied for a particular $\epsilon_i > 0$ (with positive μ), contributions from the negative branch of the spectrum $\epsilon_i' < 0$ may violate the condition for nondegeneracy. Nevertheless, the fact that there is a lower limit to the negative branch of the Dirac spectrum due to the bending of the underlying band structure opens the possibility of nondegeneracy. Considering gapped Dirac materials (eg: gapped Graphene, Group VI Dichalcogenides, etc.), it is well known that the "freeze-out"

of carriers, a sharp reduction of effective density, does occur under appropriate extrinsic conditions of heavy n-type doping by donor impurity atoms and temperature. This phenomenon has been described in terms of impurity electrons being recaptured by donors and is discussed in detail in several references [19], [20], [21]. Illustrations of freeze-out in ordinary semiconductors are provided in Figs. 1 and 2 as follows: Fig. 1 exhibits the sharp diminution of effective carrier density in n-type Si as a function of temperature, indicating the appropriateness of the low density approximation considered here. Fig. 2 exhibits the temperature dependence of the Fermi level (chemical potential) for n-type Ge (with typical values of the donor binding energy E_b), clearly indicating its descent into negativity. Both of these illustrated features correspond to the low density nondegenerate equilibrium population statistics under discussion here, with the advent of an associated negative chemical potential. And the chemical potential can be further lowered by putting the Dirac material in contact with a material having an even lower chemical potential, as discussed above. It should also be noted that such freeze-out has been observed in Landau quantized extrinsic semiconductors ("magnetic freeze-out") [22].

In summary, there are mechanisms that suggest that Dirac materials, like ordinary semiconductors, under appropriate extrinsic conditions of heavy doping and temperature, may exhibit freeze-out and sufficiently negative chemical potential to be in the nondegenerate statistical equilibrium regime. Of course, the details depend on the particular Dirac material and the value of $-E_{\min}$ for the real lower bound of the Dirac energy spectrum, and on the donor binding energy E_b (and on magnetic field strength), etc., but the existing mathematical description in the literature [23] will be helpful in the requisite analysis.

REFERENCES

[1] N. J. M. Horing, *Quantum Statistical Field Theory*. Oxford, U.K.: Oxford Univ. Press, 2017.

[2] P. C. Martin and J. Schwinger, "Theory of many particle systems," *Phys. Rev.*, vol. 115, 1959, Art. no. 1342.

[3] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd ed. Oxford, U. K.: Pergamon Press, 1980.

[4] M. W. Zemansky, *Heat and Thermodynamics*, 3rd ed. New York, NY, USA: McGraw Hill, 1951.

[5] M. Katsnelson, *Graphene: Carbon in Two Dimensions*. Cambridge, U.K.: Cambridge Univ. Press, 2012.

[6] H. Aoki and M. S. Dresselhaus, *Physics of Graphene*. Berlin, Germany: Springer, 2013.

[7] E. L. Wolf, *Graphene: A New Paradigm in Condensed Matter and Device Physics*. London, U.K.: Oxford Univ. Press, 2013.

[8] N. J. M. Horing, "Aspects of the theory of graphene," *Trans. Roy. Soc. A*, vol. 368, 2010, Art. no. 5525.

[9] M. J. S. Spencer, *Silicene*. Berlin, Germany: Springer, 2016.

[10] G. K. Ahluwalia, *Applications of Chalcogenides: S., Se, Te*. Berlin, Germany: Springer, 2017.

[11] S. Q. Shen, "Topological insulators," Berlin, Germany: Springer, 2012.

[12] J. D. Malcom and E. J. Nicol, "Frequency dependent polarizability, plasmons and screening in a 2D pseudospin 1 dice lattice," *Phys. Rev.*, vol. B93, 2016, Art. no. 165433.

[13] T. O. Wehling, A. M. Black-Shaffer, and A. V. Balatsky, "Dirac materials," *Adv. Phys.*, vol. 63, pp. 1–7, 2014.

[14] J. Wang, S. Deng, Z. Liu, and Z. Liu, "The rare 2D materials with dirac cones," *Nat. Sci. Rev.*, vol. 2, pp. 22–39, 2015.

[15] Reference 1, Section 5.1, Eq.(5.1.27).

[16] N. J. M. Horing and S. Y. Liu, "Green's function for a graphene sheet and quantum dot in a normal magnetic field," *J. Phys. A: Math. Theor.*, vol. 42, 2009, Art. no. 225301.

[17] N. J. M. Horing, "Landau quantized dynamics and spectra for group-VI dichalcogenides including a model quantum wire," *AIP Adv.*, vol. 7, 2017, Art. no. 065316.

[18] N. J. M. Horing, "Landau quantized dynamics and spectrum of the diced lattice," *J. Phys.: Condens. Matter*, vol. 33, 2020, Art. no. 015302.

[19] R. Enderlein and N. J. M. Horing, *Fundementals of Semiconductor Physics and Devices*. Singapore: World Scientific, 1997.

[20] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*. Berlin, Germany: Springer, 1984.

[21] V. L. Bonch-Bruevich and S. G. Kalashnikov, *Halbleiterphysik*. Berlin, Germany: Deutcher Verlag der Vissenshaften, 1982.

[22] M. I. Dyakonov, A. L. Efros, and D. L. Mitchell, "Magnetic freeze-out of electrons in extrinsic semiconductors," *Phys. Rev.*, vol. 180, 1969, Art. no. 813.

[23] Reference 19, Section 4.4.4.