tion of the absorption probability for a varying external magnetic field shows, that in the limit of long waves, it is completely confined to the spin waves. With increasing q the absorption is shifted in favour of the particle-hole excitations.

Silin's result for the spectrum is different. This is due to the neglect of the particle interaction in shifting the Fermi spheres.

A more detailed investigation will be presented in a forth-coming paper.

The author wishes to thank Professor W. Brenig for suggesting the problem and many helpful discussions, and the Deutsche Forschungsgemeinschaft for a grant.

References

1) L.D. Landau, J. Exptl. Theor. Phys. (USSR) 5 (1957) 101.
2) V.P. Silin, J. Exptl. Theor. Phys. (USSR) 6 (1958) 945.
3) D. Hone, Phys. Rev. 125 (1962) 1494.

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THE WIGNER DISTRIBUTION FUNCTION IN QUANTUM STATISTICS AND THE APPLICATION TO SECOND VIRIAL COEFFICIENTS

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Received 26 October 1963

From the knowledge of the distribution function one gets - as is well known - all desired thermodynamical properties of a classical system.

For quantum statistics Wigner [1] found a function which has some pertinent features of a distribution function. This Wigner distribution function (W.d.f.) is defined as a Fourier transform of the density matrix ρ in the following manner

$$f_{\mathrm{W}} = \left(\frac{1}{\hbar\pi}\right)^{3N} \int \dots \int \exp\left(\frac{2\mathrm{i}}{\hbar} p \cdot Y\right) \rho(q+Y,\ q-Y)\, \mathrm{d}Y , \tag{1}$$

p, (q): $3N$ dimensional momenta (coordinate) vector. The $3N$ dimensional integration extends over all space.

In the last years the W.d.f. frequently has been applied to problems in equilibrium statistical mechanics as well as in non-equilibrium statistical mechanics, e.g. refs. [2,3]. For that reason some further terms of the W.d.f. should be evaluated which are important for systems with large quantum effects. We use a method of Oppenheim and Ross [4]. From the Bloch equation for the density matrix ρ one gets with (1) the following equation

$$\frac{\partial f_{\mathrm{W}}(q,p;\beta)}{\partial\beta} = \left(\frac{\hbar^2}{8m}\nabla_q^{\,2} - \frac{p^2}{2m}\right) f_{\mathrm{W}}(q,p;\beta) - \cos\left(\tfrac{1}{2}\hbar\nabla_{q'}\cdot\nabla_p\right) U(q') f_{\mathrm{W}}(q,p;\beta) . \tag{2}$$

$\nabla_{q'}$ operates on q' only; $\beta = (kT)^{-1}$. This equation can be solved by the series expansion:

$$f_{\mathrm{W}}(q,p;\beta) = f_{\mathrm{cl}} \sum_{n=0}^{\infty} h^{2n}\, \Phi_n(q,p;\beta), \quad f_{\mathrm{cl}} \sim \mathrm{e}^{-\beta\left(\frac{p^2}{2m}+U\right)} . \tag{3}$$

U: potential energy. As far as we know, in the literature only the expansion coefficient Φ_1 is given in the general form for $3N$ dimensions, and Φ_2 for one dimension [1,5]. We have calculated Φ_2 and Φ_3 in the general form [6], but for the sake of brevity here we will publish the W.d.f. for one dimension only:

$$f_{\mathrm{W}}(q,p;\beta) = f_{\mathrm{cl}}\Big[1+\frac{\hbar^2\beta^2}{8m}\{U^{\mathrm{II}}(-1+\tfrac{1}{3}\frac{p^2}{m}\beta)+\tfrac{1}{3}U^{\mathrm{I}\,2}\beta\}+\frac{\hbar^4\beta^3}{1920\,m^2}\{U^{\mathrm{IV}}(-15+10\frac{p^2}{m}\beta-\frac{p^4}{m^2}\beta^2)$$
$$+U^{\mathrm{III}}U^{\mathrm{I}}\beta(20-4\frac{p^2}{m}\beta)+U^{\mathrm{II}}U^{\mathrm{I}\,2}\beta^2(-18+\frac{10}{3}\frac{p^2}{m}\beta)+U^{\mathrm{II}\,2}\beta(25-18\frac{p^2}{m}\beta+\frac{5}{3}\frac{p^4}{m^2}\beta^2)+U^{\mathrm{I}\,4}\,\tfrac{5}{3}\beta^3\}$$
$$+\frac{\hbar^6\beta^4}{46\,080\,m^3}\{U^{\mathrm{VI}}(-15+15\frac{p^2}{m}\beta-3\frac{p^4}{m^2}\beta^2+\frac{1}{7}\frac{p^6}{m^3}\beta^3)+U^{\mathrm{V}}U^{\mathrm{I}}\beta(30-12\frac{p^2}{m}\beta+\frac{6}{7}\frac{p^4}{m^2}\beta^2)$$
$$+U^{\mathrm{IV}}U^{\mathrm{II}}\beta(105-113\frac{p^2}{m}\beta+\frac{155}{7}\frac{p^4}{m^2}\beta^2-\frac{p^6}{m^3}\beta^3)+U^{\mathrm{IV}}U^{\mathrm{I}\,2}\beta^2(-39+\frac{94}{7}\frac{p^2}{m}\beta-\frac{p^4}{m^2}\beta^2) \tag{4}$$
$$+U^{\mathrm{III}\,2}\beta(42-20\frac{p^2}{m}\beta+\frac{10}{7}\frac{p^4}{m^2}\beta^2)+U^{\mathrm{III}}U^{\mathrm{II}}U^{\mathrm{I}}\beta^2(-148+\frac{432}{7}\frac{p^2}{m}\beta-4\frac{p^4}{m^2}\beta^2)$$
$$+U^{\mathrm{III}}U^{\mathrm{I}\,3}\beta^3(\frac{188}{7}-4\frac{p^2}{m}\beta)+U^{\mathrm{II}\,3}\beta^2(-61+\frac{479}{7}\frac{p^2}{m}\beta-13\frac{p^4}{m^2}\beta^2+\frac{5}{9}\frac{p^6}{m^3}\beta^3)$$
$$+U^{\mathrm{II}\,2}U^{\mathrm{I}\,2}\beta^3(\frac{479}{7}-26\frac{p^2}{m}\beta+\frac{5}{3}\frac{p^4}{m^2}\beta^2)+U^{\mathrm{II}}U^{\mathrm{I}\,4}\beta^4(-13+\frac{5}{3}\frac{p^2}{m}\beta)+U^{\mathrm{I}\,6}\,\tfrac{5}{9}\beta^5\}\Big]\,.$$

The derivatives of U are marked by Roman numerals.

From the general form we get the Slater sum by a $3N$ dimensional integration over all momenta:

$$S(q;\beta) = S_{\mathrm{cl}}\Big[1-\frac{\hbar^2\beta^2}{12m}\{\Delta U-\tfrac{1}{2}\beta(\nabla U)^2\}-\frac{\hbar^4\beta^3}{240\,m^2}\{\Delta\Delta U-\tfrac{1}{6}\beta(2\Delta(\nabla U)^2+8\,\nabla U\cdot\nabla\Delta U+5(\Delta U)^2)$$
$$+\tfrac{1}{6}\beta^2(3\nabla U\cdot\nabla(\nabla U)^2+5\Delta U(\nabla U)^2)-\tfrac{5}{24}\beta^3(\nabla U)^4\}-$$
$$-\frac{\hbar^6\beta^4}{6\,720\,m^3}\{\Delta\Delta\Delta U-\tfrac{1}{6}\beta(18\nabla U\cdot\nabla\Delta\Delta U+14\Delta U\Delta\Delta U+24\,\Delta(\nabla\nabla:\nabla_{\mathrm{I}}\nabla_{\mathrm{I}})U+17(\nabla\Delta U)^2$$
$$+6\,(\nabla\nabla\nabla:\nabla_{\mathrm{I}}\nabla_{\mathrm{I}}\nabla_{\mathrm{I}})U)+\tfrac{1}{54}\beta^2(63(\nabla U)^2\Delta\Delta U+162\,\nabla U\cdot\nabla\Delta\nabla U\cdot\nabla U+216\,\nabla U\cdot\nabla(\nabla\nabla:\nabla_{\mathrm{I}}\nabla_{\mathrm{I}})U$$
$$+306\,\nabla U\cdot\nabla\nabla U\cdot\nabla\Delta U+252\,\nabla U\cdot\nabla\Delta U\Delta U+84\,\Delta U(\nabla\nabla:\nabla_{\mathrm{I}}\nabla_{\mathrm{I}})\,U+35\,(\Delta U)^3 \tag{5}$$
$$+64\,(\nabla_{\mathrm{II}}\nabla_{\mathrm{II}}\nabla_{\mathrm{I}}:\nabla\nabla\nabla_{\mathrm{I}})\,U)-\tfrac{1}{36}\beta^3(84\,\Delta\nabla U\cdot\nabla U(\nabla U)^2+36\,(\nabla\nabla_{\mathrm{II}}\nabla_{\mathrm{III}}:\nabla_{\mathrm{II}}\nabla_{\mathrm{I}}\nabla_{\mathrm{II}})\,U$$
$$+28\,(\nabla U)^2(\nabla\nabla:\nabla_{\mathrm{I}}\nabla_{\mathrm{I}})\,U+102\,(\nabla\nabla\nabla_{\mathrm{I}}:\nabla_{\mathrm{III}}\nabla_{\mathrm{II}}\nabla_{\mathrm{I}})\,U+35\,(\nabla U)^2(\Delta U)^2+84\,\Delta U\nabla U\cdot\nabla\nabla U\cdot\nabla U)$$
$$+\tfrac{1}{72}\beta^4(84\,(\nabla U)^2\,\nabla U\cdot\nabla\nabla U\cdot\nabla U+35\,\Delta U(\nabla U)^4)+\frac{35}{6\times 72}\,\beta^5(\nabla U)^6\}\Big]\,.$$

The notation is, for example

$$(\nabla_{\mathrm{II}}\nabla_{\mathrm{II}}\nabla_{\mathrm{I}}:\nabla\nabla\nabla_{\mathrm{I}})\,U=\sum_i\sum_j\sum_k\frac{\partial^2 U}{\partial x_i\,\partial x_j}\,\frac{\partial^2 U}{\partial x_k\,\partial x_i}\,\frac{\partial^2 U}{\partial x_j\,\partial x_k}\,. \tag{6}$$

Applying (4), (5) to special cases the number of terms is reduced, of course, appreciably (see eqs. (11), (17)).

As an application the third quantum correction to the second virial coefficient $B(T)$ is calculated. For completeness we give the first terms too [7]. The second virial coefficient has the form

$$B(T) = 2\pi N\int_0^\infty (1-S(r))r^2\,\mathrm{d}r\,. \tag{7}$$

Table 1
Expansion coefficients and quantum corrections for the second virial coefficient

s	$b_0^{(s)}$	$b_1^{(s)}$	$b_2^{(s)}$	$b_3^{(s)}$
0	1.733 001 0	8.253 193 3 × 10^{-2}	-2.625 906 4 × 10^{-3}	4.199 549 3 × 10^{-4}
1	-2.563 693 4	6.301 180 4 × 10^{-2}	-7.754 452 2 × 10^{-3}	1.616 498 5 × 10^{-3}
2	-8.665 004 6 × 10^{-1}	7.627 951 4 × 10^{-2}	-1.273 524 7 × 10^{-2}	3.260 047 9 × 10^{-3}
3	-4.272 822 3 × 10^{-1}	6.791 272 2 × 10^{-2}	-1.492 659 5 × 10^{-2}	4.580 942 1 × 10^{-3}
4	-2.166 251 2 × 10^{-1}	5.081 827 4 × 10^{-2}	-1.402 440 9 × 10^{-2}	5.049 778 4 × 10^{-3}
5	-1.068 205 6 × 10^{-1}	3.352 461 3 × 10^{-2}	-1.121 039 2 × 10^{-2}	4.651 839 7 × 10^{-3}
6	-5.054 586 0 × 10^{-2}	2.001 739 0 × 10^{-2}	-7.898 541 7 × 10^{-3}	3.722 188 8 × 10^{-3}
7	-2.289 011 9 × 10^{-2}	1.100 326 5 × 10^{-2}	-5.020 488 6 × 10^{-3}	2.654 576 7 × 10^{-3}
8	-9.928 651 1 × 10^{-3}	5.634 976 7 × 10^{-3}	-2.926 099 4 × 10^{-3}	1.718 537 6 × 10^{-3}
9	-4.132 938 2 × 10^{-3}	2.712 557 6 × 10^{-3}	-1.582 651 0 × 10^{-3}	1.023 721 3 × 10^{-3}
10	-1.654 775 2 × 10^{-3}	1.235 867 4 × 10^{-3}	-8.017 114 4 × 10^{-4}	5.670 061 6 × 10^{-4}
11	-6.387 268 1 × 10^{-4}	5.358 673 4 × 10^{-4}	-3.831 123 7 × 10^{-4}	2.944 073 2 × 10^{-4}
12	-2.381 873 4 × 10^{-4}	2.221 188 3 × 10^{-4}	-1.737 165 4 × 10^{-4}	1.442 604 9 × 10^{-4}
13	-8.598 245 6 × 10^{-5}	8.834 465 2 × 10^{-5}	-7.510 105 5 × 10^{-5}	6.707 422 2 × 10^{-5}

Table 2
Data used for calculation

	$N\sigma^3$	ϵ/k	$\Lambda^* = \frac{h}{\sigma(m\epsilon)^{\frac{1}{2}}}$
He^4	10.06	10.22	2.677
H	15.12	37.02	1.730
D	15.12	37.02	1.224

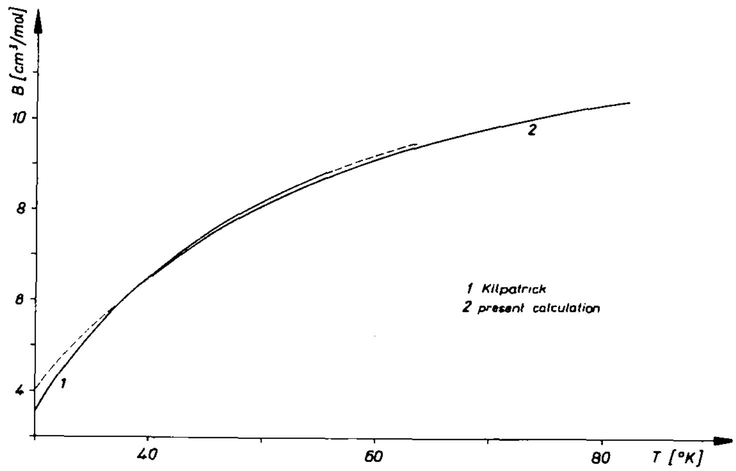

Fig. 1. Second virial coefficients of He^4.

Table 3
Contributions to second virial coefficients

	helium					hydrogen				deuterium		
T^*	B_{cl}	B_1	B_2	B_3	B_{id}	B_{cl}	B_1	B_2	B_3	B_1	B_2	B_3
1.2						-58.14				12.81	-2.97	1.28
1.8						-25.71	11.49	-2.85	1.56	5.75	-0.71	0.20
8/3	-5.00	9.07	-3.17	2.68	-0.50	- 7.52	5.70	-0.83	0.29	2.85	-0.21	0.04
4	2.43	4.92	-0.98	0.54	-0.27	3.65	3.09	-0.26	0.06	1.55	-0.06	0.01
6	6.80	2.76	-0.33	0.12	-0.15	10.23	1.74	-0.09	0.01	0.87	-0.02	0.00_2
8	8.71	1.88	-0.16	0.04	-0.10	13.09	1.18	-0.04	0.00_5	0.59	-0.01	0.00_1
12	10.29	1.12	-0.06	0.01	-0.05	15.46	0.70	-0.02	0.00_1	0.35	-0.00_4	0

N: Avogadro number. Writing $B = B_{cl} + B_1 + B_2 + B_3 + B_{id}$ and using (5) - but in polar coordinates - we find by partial integration for a general potential $U = U(r)$

$$B_{cl} = 2\pi N \int_0^\infty (1 - e^{-\beta U}) r^2 \, dr \,, \tag{8}$$

$$B_1 = 2\pi N \frac{\hbar^2 \beta^3}{12\, m} \int_0^\infty e^{-\beta U} U^{I2} r^2 \, dr \,, \tag{9}$$

$$B_2 = 2\pi N \frac{\hbar^4 \beta^4}{120\, m^2} \int_0^\infty e^{-\beta U} \{U^{II2} + 2\frac{1}{r^2} U^{I2} + \frac{10}{9}\beta \frac{1}{r} U^{I3} - \frac{5}{36}\beta^2 U^{I4}\} r^2 \, dr \,, \tag{10}$$

$$B_3 = 2\pi N \frac{\hbar^6 \beta^5}{40\,320\, m^3} \int_0^\infty e^{-\beta U} \{3\, U^{IV} U^{II} - 21 \frac{1}{r^2} U^{II2} + \frac{\beta}{3}(11 U^{III} U^{II} U^{I} - 13 \frac{1}{r} U^{II2} U^{I} - 8 \frac{1}{r^3} U^{I3})$$
$$+ \frac{\beta^2}{6}(U^{II2} U^{I2} + \frac{7}{3}\frac{1}{r^2} U^{I4}) + \frac{\beta^3}{6}\, 7 \frac{1}{r} U^{I5} - \frac{\beta^4}{72}\, 7\, U^{I6}\} r^2 \, dr \,. \tag{11}$$

As is well known, symmetry effects give rise to the following term:

$$B_{id}\,{}^{BE}_{FD} = \mp \frac{N}{16}\left(\frac{\hbar^2}{\pi m k T}\right)^{\frac{3}{2}} . \tag{12}$$

Especially for the Lennard-Jones (6-12) potential the integration over all coordinate space gives:

$$B = \frac{2\pi N \sigma^3}{3} \sum_{\nu=0}^{3} \Lambda^{*2\nu} T^{*-(3+10\nu)/12} \sum_{s=0}^{\infty} \frac{1}{s!} b_\nu^{(s)} T^{*-\frac{s}{2}}, \qquad T^* = \frac{k}{\epsilon} T \,, \tag{13}$$

with

$$b_0^{(s)} = -\frac{2^{s+\frac{3}{6}}}{4\, s!} \Gamma\left(\frac{6s-3}{12}\right) , \tag{14}$$

$$b_1^{(s)} = \frac{36s-11}{768\,\pi^2} \frac{2^{s+\frac{13}{6}}}{s!} \Gamma\left(\frac{6s-1}{12}\right) , \tag{15}$$

$$b_2^{(s)} = -\frac{3\,024 s^2 + 4\,728 s + 767}{491\,520\,\pi^4} \frac{2^{s+\frac{23}{6}}}{s!} \Gamma\left(\frac{6s+1}{12}\right) , \tag{16}$$

$$b_3^{(s)} = \frac{53\,568 s^3 + 303\,216 s^2 + 491\,076 s + 180\,615}{73\,400\,320\,\pi^6} \frac{2^{s+\frac{33}{6}}}{s!} \Gamma\left(\frac{6s+3}{12}\right) . \tag{17}$$

Table 1 gives the numerical values for these coefficients †. Using the data of the tables 1 and 2 we have calculated the terms of B for some gases. Some of these values are presented in table 3 [6]. Finally, for He^4 fig. 1 shows the conformity of our intermediate-temperature calculation with the low-temperature quantum-mechanical calculation of Kilpatrick [8].

The author is indebted to Professor Vojta for the suggestion of the theme and for valuable advice during the work.

1) E. Wigner, Phys. Rev. 40 (1932) 749.
2) G. Vojta, Z. phys. Chem. 220 (1962) 379.
G. Vojta, R. Haberlandt, Mber. Dt. Akad. Wiss. 3 (1961) 278.
3) H. Mori, I. Oppenheim, J. Ross, in: Studies in Statistical Mechanics, ed. J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962) Vol. I, p. 217 (further references).
4) I. Oppenheim, J. Ross, Phys. Rev. 107 (1957) 28.
5) G. Vojta, Ann. Physik 9 (1962) 337.
6) R. Haberlandt, Z. phys. Chem., to be published.
7) J. de Boer, Dissertation Amsterdam 1940 (further references).
8) J. E. Kilpatrick et al., Phys. Rev. 94 (1954) 1103.

† The values in the literature show some mistakes.