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ON THE SECOND ORDER VIRIAL COEFFICIENT AND THE RELATIONSHIPS BETWEEN QUANTUM AND CLASSICAL STATISTICS AND SCATTERING*

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ABSTRACT

We clarify some aspects of the relationship between quantum statistical mechanics and scattering theory, which show up in their simplest form in tne behaviour of the second-order virial coefficient b_2. For this purpose we derive a new representation for b_2. The relationship with classical statistical mechanics is also illuminated by a recently obtained formula for the difference between the classical and quantum second order virial coefficients which allows the determination of the leading quantum correction to b_2. The several approaches represent alternative ways of implementing the cancellation of divergences in b_2.

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In a recent letter[1)] some paradoxes were discussed, which bear on the relationship between scattering theory (s.t.) and quantum statistical mechanics (q.s.m.). They show up most clearly in the bahviour of the second-order virial coefficient b_2. The solution proposed in ref. 1) required modifications in some standard formulas of scattering theory.

The purpose of this letter is two-fold: firstly, to clarify these issues without any changes in the formal theory of scattering. This clarification hinges on the somewhat subtle cancellation of divergences occurring in b_2. Secondly, we discuss three different approaches to implement this cancellation, thereby computing b_2. The first one is a new formula for b_2 along the lines of s.t., the second one is more in the spirit of q.s.m. and involves a more careful analysis of the thermodynamic limit. The third one is a new formula for the difference between classical and quantum virial coefficients in terms of functional integrals, which was derived in a mathematically rigorous way in ref. 2). Here we are less formal as concerns mathematical rigor, but emphasize the fact, not done in ref. 2), that this formula is also very useful for the eminently practical purpose of computing the first quantum correction to b_2.

Let $H = H_0 + V$ denote the Hamiltonian of relative motion of two particles, H_0 the kinetic energy and V the interaction potential. The (infinite-volume) second-order virial coefficient is, up to a constant

$$b_2 = \mathrm{tr}\left(e^{-\beta H} - e^{-\beta H_0}\right) \tag{1}$$

whenever $(e^{-\beta H} - e^{-\beta H_0})$ is in the trace-class[2]. Suppose H has no bound states and let Ω be the (unitary) Moller operator[3]. Then

$$e^{-\beta H} = \Omega e^{-\beta H_0} \Omega^{\dagger} \tag{2}$$

and hence, by (1) and cyclicity of the trace, it follows that $b_2 = 0$! The solution to this paradox proposed in ref. 1) involved modifying standard formulas of s.t. such as (2). Nevertheless, (2) is rigorously true[4]. However, in spite of this there is no paradox because the argument relies implicity on the formal splitting $b_2 = (\mathrm{tr}\, e^{-\beta H} - \mathrm{tr}\, e^{-\beta H_0})$ which is not allowed because $e^{-\beta H}$ (and hence also $e^{-\beta H}$ if $|b_2| < \infty$) is not trace-class. This is easy to see if one remembers that $e^{-\beta H}$ is a kernel operator with the "Poisson kernel"

$$P_\beta(\vec{x},\vec{y}) \equiv (e^{-\beta H_0})(\vec{x},\vec{y}) = (2\pi\beta)^{-3/2} \exp(-|\vec{x}-\vec{y}|^2/2\beta) \tag{3}$$

and $\mathrm{tr}\, e^{-\beta H_0} = \int d\vec{x}\, P_\beta(x,x) = +\infty$. This is also clear if (improper) eigenfunctions $|i\rangle$ of H_0 (in the notation of ref. 1)) are used to "compute" the trace:

$\mathrm{tr}\, e^{-\beta H} = \sum e^{-\beta E} \langle i|i\rangle$ but $\langle i|i\rangle = +\infty$; if

$|i+\rangle = \Omega|i\rangle$, $\mathrm{tr}\, e^{-\beta H} = \sum_i e^{-\beta E_i} \langle i+|i+\rangle$, but $\langle i+|i+\rangle = +\infty$.

However, $\mathrm{tr}(e^{-\beta H} - e^{-\beta H_0}) = \sum_i e^{-\beta E_i} [\langle i+|i+\rangle - \langle i|i\rangle]$. We might

expect that the last sum is finite due to cancellations in the expression in brackets, suggested, e.g., if one uses the Lippman-Schwinger[3] equation. Nevertheless, the rigorous proof that $|b_2| < \infty$, under reasonable conditions on the potential, is subtle[5]. Similarly, divergent diagrams arise in the three--body terms in ref. 6). As the authors of ref. 6) remark on page 366, such diagrams are manifestly absent if one uses wave--packet states, and the proper plane-wave limit may be taken in the final formulas <u>after</u> the divergences have been cancelled.

This program was partially carried out for b_2 in ref. 6), pg. 349. We now present a more complete discussion, including a new expression for b_2. For this purpose, we use the following relation, derived and discussed in ref. 7)

$$b_2 = -\frac{1}{2\pi i} \int_C dz\, e^{-\beta z}\, \mathrm{tr}\left[G^{(+)}(z) - G_0^{(+)}(z)\right] \tag{4}$$

Above, $G^{(+)}(z) \equiv (z - H + i\varepsilon)^{-1}$, $G_0(z) \equiv (z - H_0 + i\varepsilon)^{-1}$ and C is a contour of integration enclosing the spectrum of H, as usual in s.t.. Since $G(z) = G_0(z) + G_0(z)T(z)G_0(z)$, with $T(z) = V + VG_0(z)T(z)$, we have

$$b_2 = -\frac{1}{2\pi i} \int_C dz\, e^{-\beta z}\, \mathrm{tr}\left[G_0^{(+)}(z)\, T(z)\, G_0^{(+)}(z)\right] \tag{5}$$

Further reduction of (3) may be accomplished through use of the following relation, obtained using the manipulations of ref. 8):

$$G_0^{(+)}(z)\, T(z)\, G_0^{(+)}(z) = \int_0^1 d\lambda\; G_{(\lambda V)}^{(+)}(z)\, V\, G_{(\lambda V)}^{(+)} \tag{6}$$

where $G_{(\lambda V)}^{(+)}(z)$ is the Green function corresponding to the Hamiltonian $(H_0+\lambda V)$, which satisfies the equation

$$G_{(\lambda V)}^{(+)}(z) = G_0^{(+)}(z) + G_0^{(+)}(z)\; \lambda V\; G_{(\lambda V)}^{(+)}(z) \tag{7}$$

We obtain finally the announced formula

$$b_2 = -\frac{1}{2\pi i}\int_0^1 d\lambda \int_C dz\, e^{-\beta z}\, \mathrm{tr}\left[G_{(\lambda V)}^{(+)}(z)\, V\, G_{(\lambda V)}^{(+)}(z)\right] \tag{8}$$

It is not difficult to show (using, e.g., the methods of ref. 5), Chap. 2)) that $(G_{(\lambda V)}^{(+)}(z)\, V\, G_{(\lambda V)}^{(+)}(z))$ is trace-class for each $z \in C$, and the function $(e^{-\beta z})$ provides the necessary decay along the spectrum of H_λ. This formula also shows clearly that in general $b_2 \neq 0$ unless $V = 0$. Incidentally, at a purely formal level, one may, if so wishes now introduce the "Möller operator" $\Omega_{(\lambda V)}^{(+)}(z)$, to rewrite the trace as $\mathrm{tr}\left[G_0^{(+)}(z)\,\Omega_{(\lambda V)}^{(+)\dagger}(z)\, V\, \Omega_{(\lambda V)}^{(+)} G_0^{(+)}(z)\right]$ when no bound states are present.

We now discuss two alternative approaches to

implement the cancellation of divergences in b_2 more explicitly and thereby computing b_2 in certain limiting situations. In the first one, we recall that b_2 is the limit of the corresponding quantities in finite volume. Our approach here differs from the more recent discussion[18] in an essential way. In fact, we disagree with some points in the "scattering theory in finite volume" proposed in ref. 18): in finite volume the spectra of H and H_0 are both entirely discrete and the Møller wave operators do not exist[19].

We shall use for the purpose of illustration the one-dimensional system of bosons with repulsive delta function interaction solved by Lieb and Liniger[9] and whose thermodynamics was discussed by Yang and Yang[10]. The N body Hamiltonian is

$$H_{L,c}^{(N)} = -\sum_{i=1}^{N} \frac{\partial^2}{\partial x_i^2} + 2c \sum_{i>j} \delta(x_i - x_j) \tag{9}$$

in a periodic box of length L. For the two-body problem the quasi momenta k_1, k_2 in Bethe's hypothesis[9,10] satisfy

$$k_1 = k_1^{(0)} + \frac{1}{L}\,\theta_c(k_1-k_2) \tag{10a}$$

$$k_2 = k_2^{(0)} + \frac{1}{L}\,\theta_c(k_1-k_2) \tag{10b}$$

where $\vartheta_c(k) \equiv -2\tan^{-1}(k/c)$ and the $k_i^{(0)} = (2\pi/L)\, I_{k_i}$, with

$I_{k_i} = n_{k_i} + \frac{1}{2}$, with the n_{k_i} integers are the quasi-momenta corresponding to the problem with $c = \infty$ (impenetrable bosons in one dimension[11]). Since the density of each of the $k_i^{(0)}$ equals the free density $L/(2\pi)$, it may be easily verified that the 2nd order virial coefficient corresponding to the problem with $c = \infty$ is zero. We see from (10) that the total momentum $k_1 + k_2 = k_1^{(0)} + k_2^{(0)}$. We may therefore consider

$$b_{2,L} = \mathrm{tr}\left(e^{-\beta H^{(2)}_{L,c}} - e^{-\beta H^{(2)}_{L,c=\infty}}\right) \tag{11}$$

where $H^{(2)}_{L,c}$ and $H^{(2)}_{L,C}$ are the respective Hamiltonians of relative motion, with energy eigenvalues equal to $k^2/2$, where the corresponding $k = k_1 - k_2$ satisfy by (6)

$$k = \frac{2}{L}\,\theta_c(k) + k^{(0)} \tag{12}$$

We now split one-dimensional configuration k-space into cells i of length $\Delta_{i,L}k$ equal to the splitting $\Delta k^{(0)} = (2\pi)/L$ between successive $k^{(0)}$ values (the lengths need to be equal, nor exactly equal to $k^{(0)}$, but just of that "order"). Then

$$b_{2,L} = \lim_{L\to\infty} \sum_i e^{-\beta \bar{k}_i^2/2}\left[\rho_c(\bar{k}_i) - \rho_{c=\infty}(\bar{k}_i)\right]\Delta_{c,L}k \tag{13}$$

where $\bar{k}_i$ are arbitrary points in the cells i, and ρ_c (resp. $\rho_{c=\infty}$) denote the densities of the points k (resp. $k^{(0)}$). Clearly $\rho_c(\bar{k}) = 1/\Delta k(\bar{k})$, where Δk, the "splitting between two successive k values around $\bar{k}$", depends on $\bar{k}$, and

$$\rho_c(\bar{k}) - \rho_{c=\infty}(\bar{k}) = \frac{1}{\Delta k(\bar{k})} \cdot \frac{1}{\Delta k^{(0)}} =$$

$$= \left(1 - \frac{2c}{L}\,\theta'(\bar{k})\right)\Delta k_0^{-1} - \Delta k_0^{-1} = -\frac{2c}{L}\,\theta'(\bar{k})\,\Delta k_0^{-1}$$

$$= -\frac{c}{\pi}\,\theta'(\bar{k}) \tag{14}$$

Hence, by (10), (12) and (13)

$$b_2 = -\frac{c}{\pi}\int_{-\infty}^{\infty} dk\; e^{-\beta k^2/2}\;\theta'(k) \tag{15}$$

note that there is a cancellation of length factors in (9). Since $\theta(k)$ is essentially a phase shift[12], (10) equivalent to the well-known formula of Beth and Uhlenbeck[13,14] in higher dimensions, and indeed the method in refs. 13,14) is similar: there the system is enclosed in a "sphere of large radius". The only difference is that in higher dimensions a series involving all phase-shifts $\delta_\ell(k)$ occurs ($\ell = 0,1,2,\ldots$). The bounds on $\delta_\ell(k)$ in ref. 15) may be used to study convergence or asymptotic character or this series.

The volume divergences in the quantum virial series[16] are disposed of by the linked cluster theorem[14,16]. Nevertheless, convergence of the series itself may be expected only in the "classical limit" where the thermal wave-length is much smaller than the average particle distance and of a "typical length of the potential"[14]. This question was studied in a mathematically rigorous way in ref. 2), where some of these statements were made precise. There a new formula for the difference b_2 between b_2 and its classical analogue b_2 was proved for V sufficiently smooth and of rapid decrease at infinity[2]:

$$\Delta b_2 = b_2 - b_2^{cl.} = \frac{1}{2}\int d^3x\, e^{-\beta V(x)} E_{0,x;\beta,x}\left\{1-\exp\left[-\int_0^\beta ds\left(V(\omega(s))-V(x)\right)\right]\right\} \tag{16}$$

where $E_{0.x;t.x}$ denotes expectation with respect to the measure corresponding to "Brownian bridge"[2,5], i.e., essentially, to Brownian paths "which leave x at time zero and return to x at time β". We may write $\omega(s) = x + b(s)$, where $b(s)$ is a Brownian path which leaves the origin at zero time and returns to the origin at time β, and expand $V(x+b(s)) - V(x)$ in (16) in a Taylor series. This leads to a divergent[2], but probably asymptotic series, which may be used to estimate the leading contribution to $\Delta b_2(\beta)$:

$$\Delta b_2(\beta) = -\frac{1}{2}\int d^3x\, e^{-\beta V(x)} \frac{1}{2}\sum_{i=1}^{3}\frac{\partial^2 V}{\partial x_i^2}\int_0^\beta ds\, E(b_i(s)^2) + \frac{1}{2}\int d^3x\, E_{0,x;\beta,x}\left\{\frac{\left(\int_0^\beta ds\left(\sum_{i=1}^{3}\frac{\partial V}{\partial x}\right) b_i(s)\right)^2}{2}\right\} \simeq$$

$$\simeq -\frac{\beta^4}{48}\int d^3x \sum_{i=1}^{3}\left(\frac{\partial V}{\partial x_i}\right)^2 \tag{17}$$

for β small.

Above, we used the explicit covariance formulae (see, e.g., ref. 5, pp. 40, 41).

$$E_{0,x;\beta,x}\{b_i(s)\} = 0 \qquad 0 \le s \le \beta \tag{18}$$

$$E_{0,x;\beta,x}\{b_i(s)\, b_j(t)\} = \delta_{ij}\,[s(\beta-t)] \qquad 0\le s\le t\le\beta$$

where $i,j = 1,2,3$. Notice that (17) holds only for smooth potentials: if the potential is sufficiently singular, at the origin, a different behaviour is expected[2,17], and even the sign changes[2,17]. In formula (16) a volume divergence was cancelled, by the volume term $\frac{1}{2}\int d^3x$ in $b_2^{cl}(\beta) = \frac{1}{2}\int d^3x\left(1-e^{-\beta V(x)}\right)$ (see ref. 2)) and hence in a way quite different from the previous approach. We should mention at this point that a different approach to calculation of the semiclassical limit to b_2 can be easily found using the formulation of Nussenzveig[20]. He related b_2 to the ensemble averaged time-delay, and correspondingly classical scattering theory comes into the picture in a very natural way. Details of this alternative approach will be published elsewhere[21].

In conclusion, we clarified some conceptual issues regarding the relationship between quantum statistical mechanics, scattering theory and classical statistical mechanics, on the bases of the behaviour of the second order virial coefficient. It would be interesting to find a unified treatment of these issues which is also applicable to the higher order coefficients. Part of this program (concerning the relationship of q.s.m. to s.t.) has been achieved in ref. 6).

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