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A remark on the second virial coefficient in the quantum Lorentz model

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Abstract. We calculate the second virial coefficient of the quantum Lorentz gas with point interaction. It can be evaluated in closed form for arbitrary strength of the interaction. Particular attention is given to the critical coupling which gives rise to a zero-energy resonance. Point interactions satisfy a modified Levinson's theorem; as a consequence we show that there is no cancellation between the bound state and the scattering contributions in the high-temperature expansion of the second virial coefficient, contrary to the regular potentials case. We also derive high- and low-energy sum rules for the point interaction. As an application of the sum rules we rederive a high-temperature expansion for the second virial coefficient.

1. Introduction

The S-matrix formulation of statistical mechanics through the virial expansion [1] has its origin in the work of Uhlenbeck and Beth [2] and Gropper [3] in the late 1930s. The approach proved particularly fruitful and has been extensively developed ever since. Today the method is well understood in the case of regular potentials [4, 5]. However, in the case of singular interactions some work remains to be done. One interesting singular interaction not covered by available results on regular potentials is the zero-range or delta potential. In this paper we compute the second virial coefficient for the Lorentz gas with a non-relativistic zero-range interaction. This sort of interaction has been studied since the 1930s. For an extensive bibliography we refer the reader to [6].

In the case of three dimensions a δ-function potential is not a small perturbation of the Laplacian and we have to renormalise it. The formal Hamiltonian is

$$H = -\Delta + \lambda\delta(x).$$

Here we set $\hbar = 2m = 1$ and δ is Dirac's delta function. To define H as a self-adjoint operator on $L^2(R^3)$, we approximate it by a sequence

$$H_\alpha = -\Delta + \lambda_\alpha |g_\alpha\rangle\langle g_\alpha|$$

of well defined Hamiltonians where g_α are appropriately chosen form factors. We renormalise by adjusting the coupling constant λ_α of the approximating potentials so that the two-body scattering length a is fixed.

In §§ 1 and 2 we describe our model. In §§ 3 and 4 we carry out the renormalisation of the approximating Hamiltonians with separable potentials while keeping the scattering length fixed. In § 5 we calculate the second virial coefficient in terms of the temperature and the scattering length of the underlying two-body process. We arrive at an explicit form for the second virial coefficient including the case where we have a two-body zero-energy resonance. This situation is particularly interesting: the resonance results in the three-body Efimov effect (an infinite number of bound states in the three-body problem when the two-body interactions have zero-energy resonances). The behaviour of the second and third cluster coefficients in the 'Efimov limit' for the Lorentz model with short-range interaction (with a coupling constant adjusted to produce a zero-energy resonance) has been studied in [4]. It was found that the divergence from the three-body bound state contribution cancels with the continuum contribution. In § 6 we derive high- and low-energy sum rules for the delta potential and we find there is no cancellation between the bound state and the scattering contributions in the second virial coefficient when the interaction is described by a delta potential. Finally we conclude by comparing our results with the previous results on separable and local potentials.

2. The Lorentz model

The model we consider is the quantum mechanical Lorentz gas where M 'light' particles without mutual interactions and in equilibrium at temperature T are moving randomly and independently of each other around N stationary 'heavy' scattering centres (randomly distributed) in a large box of volume $\Omega = L^3$ in $\mathbb{R}^3$.

The Hamiltonian of our system is given by

$$H_N = H_0 + V_N \tag{2.1}$$

where

$$H_0 = \sum_{i=1}^{M} \frac{p_i^2}{2m} \tag{2.2}$$

is the kinetic energy of the light particles (p_i is the momentum operator of a light particle and m its mass) and

$$V_N = \sum_{i=1}^{M} V_i(r_i). \tag{2.3}$$

Here

$$V_i(r_i) = \sum_{j=1}^{N} V(r_i - R_j) \tag{2.4}$$

is the total potential energy due to the N scatterers, i.e. is the sum of the individual light–heavy interactions.

3. The delta potential

As mentioned in the introduction we will consider a zero-range or point interaction between the light and the heavy particles. We are interested in the following potential V:

$$V\psi(x) = \lambda\delta(x)\psi(x)$$

where δ is the Dirac measure. We should note that a Hamiltonian with a δ-function potential (in three-dimensional space) is not well defined except if the coupling constant is 'renormalised' to an infinitesimal value [7].

There are many discussions of the zero-range limit of quantum mechanical interactions in the literature. In particular we can describe a zero-range interaction as a boundary condition problem for the (S wave) free radial Schrödinger equation [8], we can study the zero range as the limit of local [6] or separable [9] potentials, or we can define zero-range interactions in terms of ground states [10]. Alternatively for a discussion in terms of non-standard analysis see [11]. For an overview see [6, 7].

4. A point interaction as a limit of separable interactions

The zero-range interaction can be obtained from a separable interaction in the following way. Let us consider

$$V = \lambda_\alpha |g_\alpha\rangle\langle g_\alpha| \tag{4.1}$$

where λ_α is the coupling strength constant and g_α is a Yamaguchi form factor. To obtain the δ potential in the limit, we have to impose [9] the condition

$$\lim g_\alpha(k) = 1$$

when

$$\alpha \to +\infty$$

which is fulfilled by the form factor

$$g_\alpha(k) = \langle k|g_\alpha\rangle = \frac{\alpha^2}{k^2+\alpha^2}. \tag{4.2}$$

For separable potentials the t matrix in momentum space is given by [8]

$$\langle k'|t(z)|k\rangle = \frac{g_\alpha(k')g_\alpha^*(k)}{\lambda_\alpha^{-1} - \int \mathrm{d}^3k\, G_0(z)|g_\alpha(k)|^2}. \tag{4.3}$$

Let us define the resolvent for the non-interacting system by

$$G_0(z) = (z - H_0) = (z-k^2)^{-1} \tag{4.4}$$

and

$$D_\alpha(z) = \lambda_\alpha^{-1} - \int \mathrm{d}^3k\, G_0(z)|g_\alpha(k)|^2. \tag{4.5}$$

Since

$$D(z) = \lim_{\alpha\to+\infty} D_\alpha(z) \tag{4.6}$$

does not exist for λ_α constant we choose λ_α such that

$$D_\alpha(0) = D_0 \tag{4.7}$$

where D_0 is a fixed constant that later we will relate to the inverse of the scattering length. Then we obtain the infinitesimal coupling constant

$$\lambda_\alpha = (D_0 - \pi^2\alpha)^{-1} \tag{4.8}$$

but the t matrix remains perfectly finite and well defined in the limit as $\alpha \to +\infty$; in the limit we obtain

$$\langle k'|t(z)|k\rangle = (D_0 - 2\pi^2\sqrt{-z})^{-1} \tag{4.9}$$

i.e.

$$\langle k'|t(z)|k\rangle = (D_0 + 2\pi^2 \mathrm{i}\kappa)^{-1} \tag{4.10}$$

if we map the two Riemannian sheets of $\sqrt{-z}$ on one plane by using the transformation $\sqrt{-z} = -\mathrm{i}\kappa$. From (4.10) we see that we have a bound state when

$$\kappa = \mathrm{i}D_0/2\pi^2 \tag{4.11}$$

and the κ pole is in the upper half-plane, i.e. if $D_0 > 0$.

The S matrix for the S wave zero-range potential is given by [8]

$$S = \frac{c + \mathrm{i}\kappa}{c - \mathrm{i}\kappa} \tag{4.12}$$

where c is the inverse of the scattering length, i.e. $c = -1/a$. It is related to the t matrix by

$$S = 1 - 4\pi^2\kappa \mathrm{i} t \tag{4.13}$$

with

$$t = \langle k|t(\kappa^2)|k\rangle.$$

Comparing (4.12) with (4.13) we obtain

$$\langle k'|t(z)|k\rangle = \frac{1}{2\pi^2(\mathrm{i}\kappa - c)} \tag{4.14}$$

and comparing with (4.11) we conclude that

$$D_0 = -2\pi^2 c. \tag{4.15}$$

We should remark that the approximating potentials are always attractive as the infinitesimal coupling constant λ_α given by (4.8) is always negative when $\alpha \to +\infty$. From (4.11) and (4.14) we can see that $c < 0$ means that we have a potential attractive enough to support a bound state and the case $c > 0$ corresponds to a weakly attractive potential with an anti-bound state of energy $E = -c^2$ (in the second sheet). In particular for $c = 0$ there is a zero-energy resonance which corresponds to the Efimov limit.

5. The second virial coefficient

Following [4] the second virial coefficient is given by

$$B = -\Lambda^3 \mathscr{L}^{-1}(\mathrm{Tr}\, G_0^2 t) \tag{5.1}$$

where $\mathscr{L}^{-1}$ denotes the Watson transformation [12] and t is given by all connected diagrams of the light particle with one scatterer. Here

$$\Lambda = (4\pi\beta)^{1/2} \tag{5.2}$$

and the trace is taken in the light particle space [13]. We should remark that it is sufficient to consider a single light particle moving around the heavy ones since we are considering identical, independent and distinguishable light particles with the same mass m.

From (5.1) we can write

$$B = -\Lambda^3[\theta(-c)\,e^{-\beta E_0} - \frac{1}{\pi}\int_0^{+\infty} dE\, e^{-\beta E}\,\mathrm{Im\,Tr}\,G_0^2(E^+)t(E^+)] \tag{5.3}$$

where E_0 is the binding energy

$$E_0 = \kappa^2 = -\frac{D_0^2}{4\pi^4} = -c^2 \qquad \text{and} \qquad E^+ = E + i\varepsilon \tag{5.4}$$

and the first term on the RHS of (5.3) represents the bound state contribution. We have

$$\begin{aligned}\mathrm{Im\,Tr}[G_0^2(E^+)t(E^+)] &= \mathrm{Im}\int d^3k \frac{1}{(k^2-z)^2}\,t(z)\\ &= 4\pi\,\mathrm{Im}\left(t(z)\int_0^{+\infty} dk \frac{k^2}{(k^2-z)^2}\right)\end{aligned} \tag{5.5}$$

which by standard complex integration gives

$$\begin{aligned}\mathrm{Im\,Tr}[G_0^2(E^+)t(E^+)] &= \pi\,\mathrm{Im}\left(t(z)\frac{\pi}{\sqrt{-z}}\right)\\ &= -\frac{1}{2\sqrt{E}}\frac{c}{c^2+E}.\end{aligned} \tag{5.6}$$

Inserting (5.6) and (5.4) in (5.3), we have

$$B = -\Lambda^3\{\theta(-c)\,e^{c^2\beta} + \tfrac{1}{2}(\mathrm{sgn}\,c)\,e^{c^2\beta}[1-\phi(c^2\beta)^{1/2}]\} \tag{5.7}$$

where ϕ is the probability integral [14]

$$\phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x dt\, e^{-t^2}$$

and the functions θ and sgn are defined by

$$\begin{aligned}\theta(c) &= \begin{cases} 1 & c \geqslant 0 \\ 0 & c < 0 \end{cases}\\ \mathrm{sgn}\, c &= \begin{cases} 1 & c \geqslant 0 \\ -1 & c < 0. \end{cases}\end{aligned} \tag{5.8}$$

Equation (5.7) allows us to study the behaviour of the second virial coefficient at low and high temperatures. From this expression for B we see that if the interaction is attractive enough to support a bound state ($c<0$) the behaviour of B at low temperatures is

$$B \simeq -8\pi^{3/2}\beta^{3/2}\,e^{c^2\beta} - \frac{4\pi\beta}{c} + O(1) \tag{5.9}$$

since asymptotically [14]

$$\phi(\sqrt{x}) = 1 - \frac{1}{\pi}e^{-x}\sum_{k=0}^{n-1}(-1)^k\frac{\Gamma(k+\frac{1}{2})}{x^{k+1/2}} + \frac{e^{-x}}{\pi}R_n \tag{5.10}$$

where

$$|R_n| \leq \frac{\Gamma(n+\frac{1}{2})}{|x|^{n+1/2}\cos\frac{1}{2}\gamma} \qquad x = |x|\,e^{i\varphi} \qquad \varphi^2 < \pi^2.$$

If we have a weakly attractive interaction ($c > 0$) we conclude

$$B \simeq -\frac{4\pi\beta}{c} + O(1). \tag{5.11}$$

On the other hand at high temperatures (5.7) becomes

$$B \simeq -\Lambda^3\left[\theta(-c)\,e^{c^2b} + \tfrac{1}{2}(\operatorname{sgn} c)\left(e^{c^2b} - \frac{2}{\sqrt{\pi}}\sqrt{c^2\beta}\right)\right] + O(\beta^3) \tag{5.12}$$

as it is

$$\phi(x) = \frac{2}{\sqrt{\pi}}\,e^{-x^2}\sum_{k=0}\frac{2^k x^{2k+1}}{(2k+1)!!}.$$

For both $c > 0$ and $c < 0$ we obtain

$$B \simeq -4\pi^{3/2}\beta^{3/2}\,e^{c^2\beta} + 8\pi\beta^2 c + O(\beta^3). \tag{5.13}$$

In the case $c = 0$ we should note that for $c \to \pm 0$ we obtain exactly the same value, namely

$$B = -4\pi^{3/2}\beta^{3/2} \tag{5.14}$$

i.e. we have the explicit form of the second virial coefficient in the case $c = 0$ (the Efimov limit).

Remark 1. We note that if we would study the high-temperature behaviour of B considering the point interaction as the limit of a separable potential we would have [4]

$$B \simeq 8\pi^{3/2} l\alpha^2\beta^{5/2} \qquad l = \lambda\alpha^{-3}\pi^2 \tag{5.15}$$

where λ is the coupling constant. In particular, $l = -1$ is the Efimov limit and we would obtain

$$B \simeq -8\pi^{3/2}\alpha^2\beta^{5/2} \tag{5.16}$$

which is divergent for $\alpha \to +\infty$. Hence we see that we may not interchange the local ($\alpha \to +\infty$) and the high-energy limit ($\beta \to 0$). Furthermore in the local case we know [5] that

$$B = -\sum_{n=1}^{\infty} c_n \frac{(-\beta)^n}{n!} \tag{5.17}$$

where the coefficients c_n are calculated by integrating certain polynomials that are a three-dimensional generalisation of the invariants of the Korteweg–de Vries equation [15], for example,

$$c_1 = \int \mathrm{d}r\, v(r)$$

where $v(r)$ is the local interaction between the light and the heavy particles. Since the delta potential can be considered as the limit of separable or local interactions, we see from (5.13) that the exponent in the high-temperature behaviour of the second virial coefficient for a point interaction $\nu = \frac{3}{2}$, coincides neither with that for separable interactions, $\nu = \frac{5}{2}$, nor that for local potentials, $\nu = 1$.

Remark 2. From (5.7) we see that the second virial coefficient in our model is always negative which seems not to agree with the results obtained experimentally for several monatomic gases [16]. In fact, it is found that the second virial coefficient is negative at low energies, becomes zero at a certain temperature (the 'Boyle' temperature) and continues to be positive. However as our approximating potentials are always attractive (4.8) the pressure on the walls is decreasing. This agrees with the fact that when we add the first subtraction term (the second virial coefficient) in the law for ideal gases we obtain a lower pressure.

6. Higher-order Levinson's theorems for the delta potential

The higher-order versions of Levinson's theorem consist in the integration in the complex plane of the trace of the resolvent difference multiplied by a function $g(z) = z^L$. Here L can take positive or negative integer values, depending on whether we are interested in high- or low-energy sum rules. We evaluate

$$\int_c \mathrm{d}z\, g(z)\, \mathrm{Tr}\, G_0^2(z)t(z) = 0 \tag{6.1}$$

along a contour of integration composed by the contours C_j, C_η and C_γ. The contours C_j encircle the distinct eigenvalues of the Hamiltonian, C_η is defined as the set of points in the complex plane having a distance η or greater away from the positive real axis and C_γ is a circle centred at the origin with radius $\gamma \to +\infty$. If we set $g(z) = z^L$ in (6.1) the integrand is not an integrable function. As a consequence we have to consider the function

$$\mathrm{Tr}\, G_0^2(z)t(z) - \sigma_L(z) \tag{6.2}$$

where the functions σ_L are subtractions made in order to obtain an integrable function.

Since our potential is singular we cannot take over the sum rules derived for local [17] and for separable potentials [4] directly in our case (point interactions satisfy a modified Levinson's theorem). In fact, from (5.6) we obtain ($N_b = 1$)

$$\int_0^{+\infty} \mathrm{d}k^2\, \mathrm{Im}\, \mathrm{Tr}\, G_0^2 t = \pi(N_b - \tfrac{1}{2}) \tag{6.3}$$

where N_b is the number of discrete eigenstates of the Hamiltonian with eigenvalue $-\lambda_j^2 < 0$, counting multiplicity.

We remark from (5.6) that in our case the integrand in the Efimov limit ($c = 0$) is distribution valued. By Taylor's expansion technique for $|c/k| < 1$

$$\mathrm{Im}\, \mathrm{Tr}\, G_0^2(k)t(k) = -\sum_{n=1}^{\infty} (-1)^{n-1} \frac{c^{2n-1}}{2k^{2n+1}} \tag{6.4}$$

and we obtain using (5.6) and (6.3) the high-energy sum rules

$$\int_0^{+\infty} \mathrm{d}k^2\, k^{2L} \left(2\, \mathrm{Im}\, \mathrm{Tr}\, G_0^2 t + \sum_{n=1}^{L} (-1)^{n-1} \frac{c^{2n-1}}{k^{2n+1}} \right) = 2\pi(N_b - \tfrac{1}{2})(E_0)^L. \tag{6.5}$$

By applying a corresponding method to derive low-energy sum rules for a delta potential we obtain the convergent expansion for $|k/c| < 1$

$$\mathrm{Im}\, \mathrm{Tr}\, G_0^2(k)t(k) = -\sum_{n=1}^{\infty} (-1)^{n-1} \frac{k^{2n-3}}{2c^{2n-1}} \tag{6.6}$$

and

$$\int_0^{+\infty} dk^2\, k^{-2L}\left(2\,\mathrm{Im}\,\mathrm{Tr}\,G_0^2t+\sum_{n=1}^{L}(-1)^{n-1}\frac{k^{2n-3}}{c^{2n-1}}\right)=2\pi(N_b-\tfrac{1}{2})(E_0)^{-L}. \tag{6.7}$$

We should remark that if we look at the delta potential as a separable interaction we would obtain an expression similar to the high-energy sum rules derived for separable potentials [4] with $l=\pi^2\lambda\alpha$. As a consequence we see that the first subtraction term would be divergent in the limit $\alpha\to+\infty$.

7. High-temperature behaviour of the second virial coefficient

Sum rules as those derived in § 6 are of interest in nuclear scattering and statistical mechanics as they provide a relation between the number of bound states, phase shift and binding energies.

In [4, 17] it is shown that there is a cancellation between the bound state and the scattering contributions in the high-temperature expansion of the second virial coefficient in the separable and local potentials case. Here we show there is no cancellation when the interaction is described by a delta potential as an application of the sum rules derived in the previous section.

We consider now the continuum contribution B^c for the second virial coefficient

$$B^c=-\Lambda^3\left(-\frac{1}{\pi}\int_0^{+\infty} dE\, e^{-\beta E}\,\mathrm{Im}\,\mathrm{Tr}\,G_0^2t\right). \tag{7.1}$$

By partial integration with respect to E and using (6.5) we obtain

$$B^c=-\Lambda^3\left(-N_b+\tfrac{1}{2}+\frac{\beta}{\pi}\int_0^{+\infty} dE\, e^{-\beta E}\int_0^{+\infty} dE_0\,\mathrm{Im}\,\mathrm{Tr}\,G_0^2t\right). \tag{7.2}$$

By repeated partial integration and writing (6.5) as a multiple integral we obtain for the first terms of the high-temperature expansion of the second virial coefficient

$$B\simeq-8\pi^{3/2}\beta^{3/2}\left(\theta(-c)\,e^{-\beta c^2}-(N_b-\tfrac{1}{2})-\frac{\beta^{1/2}c}{\pi^{1/2}}-\beta c^2(N_b-\tfrac{1}{2})-\frac{2}{3}\frac{\beta^{3/2}c^3}{\pi^{1/2}}\right) \tag{7.3}$$

where $N_b=1$ (0) when $c<0$ ($c>0$).

We should note that (7.3) is just the high-temperature expansion of our closed form for (5.7), i.e.

$$B\simeq-4\pi^{3/2}\beta^{3/2}+8\pi\beta^2c-4\pi^{3/2}\beta^{5/2}c^2. \tag{7.4}$$

8. Conclusions and additional remarks

From (6.5) and (6.7) we can observe some differences between our sum rules and the ones derived for local [17] and separable potentials [4]. In fact even though our sum rules are very similar to the local case we should note that we have no need of a correction term for the first sum rule ($L=0$). We note that this feature is shared also by the sum rules for separable interactions. Further, the first subtraction term in the high-energy sum rules is proportional to k^{-3} and not to k^{-1} as for local potentials. We remark that this is also shared by the separable Yamaguchi form factor [18].

While there is a cancellation between the bound state and the continuum contributions in the second virial coefficient at high temperatures for regular potentials [4, 5] we see from (7.3) that, when the interaction is described by a point interaction, the bound state contribution cancels with part of the continuum contribution. In the case of zero-range interaction it is not obvious how to verify this cancellation since the bound state energy and the scattering are given in terms of the scattering length. However, we note that in (7.5) the cancellation in fractional powers in β does not occur just because of the factors $N_b - \frac{1}{2}$ instead of N_b ($N_b = 1$), which are characteristic of the modification of Levinson's theorem. Consequently there remain powers of the binding energy. As we remarked before, the leading term of the high-temperature expansion of the second virial coefficient is $\beta^{3/2}$ and not $\beta^{5/2}$ or β, characteristic of the separable or the local interactions, respectively.

The sum rules can provide us with an indication of the behaviour of the third virial coefficient in the presence of the Efimov effect. Although the bound state contribution to the third virial coefficient produces a divergence, this cancels explicitly with the continuum contribution when the interaction is an S-wave Yamaguchi potential [4]. Recently this has been seen also for local potentials [19]. As indicated above we expect only partial cancellation. It would be interesting to see the effect of this partial cancellation on the third virial coefficient in the Efimov limit.

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