Higher virial coefficients in two and three dimensions: Planck-Larkin structure and Wigner-Kirkwood expansion

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We derive three-particle higher-order sum rules in two dimensions in analogy with similar rules existing in three dimensions. We employ these rules to study the Planck-Larkin structure of the third cluster integral in the presence of three-particle processes like rearrangement scattering and breakup. In particular, in three dimensions we also show the cancellation between bound-state and continuum contributions at the Efimov point. As a byproduct we obtain a Wigner-Kirkwood-type expansion for the third virial coefficient in two and three dimensions.

I. INTRODUCTION

The two-particle Planck-Larkin partition function (PLPF) has received some new attention recently in the study of strongly coupled plasmas.[1] It is clear by now that this two-particle effective bound-state sum provides an analytic way of determining a borderline between discrete real bound states and discrete quasifree states near the continuum edge of the plasma. These quasifree states should be treated like the scattering contributions. This is known as effective lowering of the plasma continuum. In this way the PLPF has been used, e.g., to study the equation of state,[2,3] to determine occupation numbers,[4] and to look at astrophysical problems.[5,6] (For earlier work in this direction we refer to the references in Refs. 1–6 and to Ref. 7.)

A rigorous explanation for the underlying structure of the two-particle PLPF has been presented in Ref. 8, starting from a generalized Beth-Uhlenbeck representation of the second virial coefficient in terms of bound-state and scattering contributions. Using higher-order Levinson theorems[9] a cancellation is shown to exist between these bound-state and scattering contributions leading to the PLPF. As a by-product of this study, an alternative derivation of the well-known Wigner-Kirkwood expansion is obtained.

Since there exists some growing interest in the third virial coefficient in two and three dimensions, both from a theoretical and an experimental point of view (for a recent review and references, see Ref. 10), the question whether a similar Planck-Larkin (PL) formula and Wigner-Kirkwood expansion can be derived for the third and higher virial coefficients is certainly worthwhile. In this respect, the existence of a multielectron PL hydrogenic partition function has been considered by Rogers[11] in a semiclassical approach. Hoogeveen and Tjon[12] showed in a model calculation of a binary gas mixture that the divergence in the three-particle bound-state contribution to the cluster coefficient due to the Efimov effect (i.e., condensation of three-particle levels at breakup threshold due to a zero-energy bound state of some of the short-range pair interactions) is cancelled by continuum contributions. As these authors remark, their models are essentially two-particle simulations of real three-particle systems. One of their conclusions is then that it would be interesting to know whether the inclusion of three-particle processes like rearrangement, breakup, etc. would not change these results.

One of the purposes of this paper is to answer the foregoing question by studying the PLPF on a fully quantum-mechanical level starting from the three-particle sum rules that are derived in Ref. 13. Furthermore, we derive similar sum rules in two dimensions in order to look at the structure of the two-dimensional PLPF. Another aim is to obtain Wigner-Kirkwood-type expansions for the third virial coefficient in two and three dimensions.

The rest of this paper is then organized as follows. In Sec. II we review the existing results on sum rules for three-particle scattering in three dimensions and we derive their two-dimensional analogues by following a similar method. Using these rules we study in Sec. III the Planck-Larkin structure for the third cluster integral, taking into account three-particle processes like rearrangement scattering and breakup. We discuss the cancellation between bound-state and continuum contributions. We find that it is more delicate than the one for the second cluster integral and that it remains valid at the Efimov point in three dimensions. In Sec. IV we obtain Wigner-Kirkwood-type (high-temperature) expansions for the third virial coefficient in two and three dimensions.

II. THREE-PARTICLE SUM RULES IN TWO AND THREE DIMENSIONS

In Ref. 13 we have derived sum rules for three-particle scattering in three dimensions with pairwise interactions. Here we extend these results to two dimensions. We start by briefly reviewing the results of Ref. 13.

An important quantity to be studied in three-particle scattering is the connected Green's-function difference, $R_c(z)$, defined by

$$R_c(z) \equiv R(z) - R_0(z) - \sum_{\alpha=1}^{3} [R_\alpha(z) - R_0(z)] . \qquad (2.1)$$

Here $R_0(z)$, $R(z)$, and $R_\alpha(z)$ are the Green's functions for, respectively, the free Hamiltonian H_0, the total

Hamiltonian H, and the channel Hamiltonian H_α given by

$$R_0(z)=(H_0-z)^{-1},\quad H_0=-\Delta\ , \tag{2.2}$$

$$R(z)=(H-z)^{-1},\quad H=H_0+\sum_{\alpha=1}^{3}V_\alpha\ , \tag{2.3}$$

$$R_\alpha(z)=(H_\alpha-z)^{-1},\quad H_\alpha=H_0+V_\alpha\ , \tag{2.4}$$

with z the complex three-particle energy, Δ the six-dimensional Laplacian, and V_α the local short-range (not necessarily spherically symmetric) potential acting between the particles β and γ.

We are interested in the analytic behavior of these Green's functions, especially for large z. A standard method to obtain this is the Laplace transform technique (see, e.g., Ref. 14). There one starts from

$$R(z,\boldsymbol{\rho},\boldsymbol{\rho}')=\int_0^\infty d\beta\, e^{z\beta}(e^{-\beta H})(\boldsymbol{\rho},\boldsymbol{\rho}')\ ,$$
$$\mathrm{Re}\,z<\inf\{\sigma(H)\}\ , \tag{2.5}$$

where $\sigma(H)$ denotes the spectrum of H and $\boldsymbol{\rho}$ is the following six-dimensional coordinate space vector describing the position of the three particles

$$\boldsymbol{\rho}\equiv(\mathbf{x}_\alpha,\mathbf{y}_\alpha),\quad \rho^2=\frac{n_\alpha}{m_0}x_\alpha^2+\frac{\mu_\alpha}{m_0}y_\alpha^2\ , \tag{2.6}$$

with $\mathbf{x}_\alpha$ the vector separation of particle α from the center of mass of the cluster (β,γ) and $\mathbf{y}_\alpha$ the vector separation of the constituents β and γ of that cluster. The masses n_α and μ_α are the corresponding reduced masses and $m_0^2=\Pi_\alpha m_\alpha(\sum_\alpha m_\alpha)^{-1}=n_\alpha\mu_\alpha$ with m_α the mass of particle α. We remark that formulas (2.6) are invariant with respect to the choice of α. One then considers the asymptotic expansion in $\beta=1/kT$, T the temperature

$$(e^{-\beta H})(\boldsymbol{\rho},\boldsymbol{\rho}')\sim(e^{-\beta H_0})(\boldsymbol{\rho},\boldsymbol{\rho}')\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\beta^n P_n(\boldsymbol{\rho},\boldsymbol{\rho}')$$
$$\text{as } \beta\to 0\ , \tag{2.7}$$

where the free heat kernel $[\exp(-\beta H_0)](\boldsymbol{\rho},\boldsymbol{\rho}')$ has the standard form

$$(e^{-\beta H_0})(\boldsymbol{\rho},\boldsymbol{\rho}')=(4\pi q\beta)^{-3}\exp[-(4\beta q)^{-1}(\boldsymbol{\rho}-\boldsymbol{\rho}')^2]\ ,$$
$$q=\hbar^2/2m_0\ , \tag{2.8}$$

and where the coefficient functions $P_n(\boldsymbol{\rho},\boldsymbol{\rho}')$ are completely determined in terms of the potential $V=\sum_\alpha V_\alpha$. These functions P_n have been studied in detail in the literature (see the references in Ref. 9). They satisfy known recursion relations[15] and the first few have been written down explicitly (see, e.g., Ref. 14).

Combining (2.5)–(2.8) one arrives at the expansion[13]

$$R(z,\boldsymbol{\rho},\boldsymbol{\rho}')\sim\frac{\pi i}{(4\pi q)^3}\times\sum_{n=0}^{\infty}\frac{1}{n!}P_n(\boldsymbol{\rho},\boldsymbol{\rho}')\frac{1}{z^{n-2}}(z^{1/2}q^{-1/2}s/2)^{n-2}\times H_{n-2}^{(1)}(z^{1/2}q^{-1/2}s)\ , \tag{2.9}$$

where $H_m^{(1)}$ is the Hankel function of the first kind of order m and $s\equiv|\boldsymbol{\rho}-\boldsymbol{\rho}'|$. For the connected Green's-function difference (2.1) one can derive a similar expansion[13]

$$R_c(z,\boldsymbol{\rho},\boldsymbol{\rho}')\sim\frac{\pi i}{(4\pi q)^3}\times\sum_{n=2}^{\infty}\frac{1}{n!}P_n^c(\boldsymbol{\rho},\boldsymbol{\rho}')\frac{1}{z^{n-2}}(z^{1/2}q^{-1/2}s/2)^{n-2}\times H_{n-2}^{(1)}(z^{1/2}q^{-1/2}s)\ , \tag{2.10}$$

where P_n^c now denotes the following "connected" coefficient function

$$P_n^c(\boldsymbol{\rho},\boldsymbol{\rho}')=P_n(\boldsymbol{\rho},\boldsymbol{\rho}')-\sum_{\alpha=1}^{3}P_n^\alpha(\boldsymbol{\rho},\boldsymbol{\rho}')\ , \tag{2.11}$$

with P_n^α the coefficient functions occurring in R_α. In (2.10) the fact has been used that the $n=0$ term of R_c vanishes identically and that the $n=1$ term is zero because of the linearity of P_1^c in the potential. The last result is a consequence of having pairwise potentials. If there is a three-particle force (depending on both $\mathbf{x}_\alpha$ and $\mathbf{y}_\alpha$), then $P_1^c\neq 0$. We finally remark that the $n=2$ term in (2.10) is singular for $\boldsymbol{\rho}\to\boldsymbol{\rho}'$, i.e., $s\to 0$.

The sum rules are then derived on the basis of Cauchy's theorem and the analyticity properties of R_c in the complex energy plane. We start from the analytic function ($N=0,1,2,\ldots$)

$$F_N(z,\boldsymbol{\rho})\equiv z^N\left[\tilde{R}(z,\boldsymbol{\rho})-\frac{1}{(4\pi q)^3}\times\sum_{n=3}^{N+3}\frac{P_n^c(\boldsymbol{\rho})}{n(n-1)(n-2)}\frac{1}{z^{n-2}}\right]\ , \tag{2.12}$$

where $P_n^c(\boldsymbol{\rho})\equiv P_n^c(\boldsymbol{\rho},\boldsymbol{\rho})$ and where $\tilde{R}(z,\boldsymbol{\rho})$ is the diagonal value of the connected resolvent difference, viz.,

$$\tilde{R}(z,\boldsymbol{\rho})\equiv\lim_{s\to 0}\left[R_c(z,\boldsymbol{\rho},\boldsymbol{\rho}')-\frac{\pi i}{2(4\pi q)^3}P_2^c(\boldsymbol{\rho},\boldsymbol{\rho}')\times H_0^{(1)}(z^{1/2}q^{-1/2}s)\right]\ . \tag{2.13}$$

The subtraction terms $n=3,4,\ldots,N+3$ are the diagonal values of the corresponding terms in (2.10). We then integrate $F_N(z,\boldsymbol{\rho})$ along a contour in the z plane encircling the spectrum of the Hamiltonian H. In this way, we arrive at, after integrating with respect to $\boldsymbol{\rho}$ (Ref. 13)

$$\int_{-\chi_\alpha^2}^{\infty} dE\, E^N \left[2\,\mathrm{Im\,Tr}\, R_c(E+i0) - \frac{\pi}{(4\pi q)^3} \int d\rho\, P_2^c(\rho) \right] = -2\pi \sum_{j=1}^{N_3} (E_j)^N - \frac{2\pi}{(4\pi q)^3 (N+1)(N+2)(N+3)} \int d\rho\, P_{N+3}^c(\rho) , \quad (2.14)$$

with $N=0,1,2,\ldots$ and where $-\chi_\alpha^2$ is the lowest two-particle threshold, N_3 the number of three-particle bound states with respective positions E_i, and the first P_n^c are given explicitly by

$$P_2^c = 2 \sum_\alpha \sum_{\beta>\alpha} V_\alpha V_\beta , \quad (2.15)$$

$$P_3^c = 6 V_\alpha V_\beta V_\gamma + 3 \sum_\alpha \sum_{\beta\neq\alpha} V_\alpha V_\beta^2 - q \sum_\alpha \sum_{\beta\neq\alpha} V_\alpha \Delta_\rho V_\beta - q \sum_\alpha \sum_{\beta>\alpha} \nabla_\rho V_\alpha \cdot \nabla_\rho V_\beta . \quad (2.16)$$

Following a similar procedure, we now present a derivation, as far as we know for the first time, of a set of sum rules for three-particle scattering in two dimensions.

First, it is straightforward to check that the equivalent of the series (2.10) for the connected Green's function now reads

$$R_c(z,\rho,\rho') \sim \frac{-\pi i}{(4\pi q)^2} \times \sum_{n=2}^{\infty} \frac{1}{n!} P_n^c(\rho,\rho') \frac{1}{z^{n-1}} (z^{1/2} q^{-1/2} s/2)^{n-1} \times H_{n-1}^{(1)}(z^{1/2} q^{-1/2} s) , \quad (2.17)$$

where ρ,ρ' are the corresponding four-dimensional coordinate vectors and the P_n^c are still given by (2.11), (2.15), and (2.16) but with the ∇ operator now acting in four-dimensional space. Comparing with (2.10) we see that the first term, i.e., the $n=2$ term, is not singular as $s \to 0$. This will have some consequences for the structure of the sum rules.

Indeed, we can now consider directly the analytic function [compare (2.12) and (2.13)]

$$F_N(z,\rho) \equiv z^N \left[R_c(z,\rho,\rho) + \frac{1}{(4\pi q)^2} \sum_{n=2}^{N+2} \frac{P_n^c(\rho)}{n(n-1)} \frac{1}{z^{n-1}} \right] , \quad (2.18)$$

where the subtraction terms are the diagonal values of the corresponding terms in (2.17). With this function, we then perform a contour integration in the complex energy plane around the spectrum of the Hamiltonian, i.e., along the following path which is the same as for three dimensions:[13] C_η around the real axis from $\Gamma - i\eta$ to $\Gamma + i\eta$, $\Gamma > 0$, avoiding the deepest two-particle threshold, $-\chi_\alpha^2$, by a circle

$$C_\chi = [\eta \exp(i\theta) \mid \theta \in (3\pi/2, \pi/2)] ,$$

along the circle

$$C_\Gamma = [\Gamma \exp(i\theta) \mid \theta \in [\arcsin(\eta/\Gamma), 2\pi - \arcsin(\eta/\Gamma)] ,$$

and finally encircling all bound-state energy positions E_j clockwise by

$$C_j = [\epsilon_j \exp(i\theta_j) \mid \theta_j \in [0,2\pi],\ \epsilon_j \text{ sufficiently small}] , \quad 1 \le j \le N_3 .$$

Employing Cauchy's theorem,

$$\oint_C dz \int d\rho\, F_N(z,\rho) = 0 , \quad C \equiv C_\eta \cup C_\chi \cup C_\Gamma \cup \left[\sum_j C_j \right] , \quad (2.19)$$

we get, after some calculations ($N=0,1,2,\ldots$)

$$\int_{-\chi_\alpha^2}^{\infty} dE\, E^N 2\,\mathrm{Im\,Tr}\, R_c^{(2)}(E+i0) = -2\pi \sum_{j=1}^{N_3} (E_j^{(2)})^N + \frac{2\pi}{(4\pi q)^2 (N+1)(N+2)} \times \int d\rho\, P_{N+2}^{(2),c}(\rho) , \quad (2.20)$$

where we have added the superscript (2) to indicate two dimensions. The first term on the right-hand side of (2.20) stems from the bound-state singularities in R_c (C_j integrals), the second term results from the $C_\eta \cup C_\chi$ integration of the subtraction terms in F_N. Hereby we have assumed that $-\chi_\alpha^2$ is not a three-particle bound-state accumulation point. The left-hand side of (2.20) represents the $C_\eta \cup C_\chi$ integration of the Green's-function part of F_N using its reflection property. We remark that, because of our construction of F_N, the C_Γ contour gives no contribution.

These sum rules constitute higher-order three-particle Levinson theorems in two dimensions. For fixed N, they require the potential and an N-dependent number of its derivatives to be smooth enough in order to ensure the existence of the ρ integral over P_{N+3}^c. Compared with the three-dimensional results (2.14), there is no correction term in the integral on the left-hand side of (2.20) and the surface correction on the right-hand side contains P_{N+2}^c instead of P_{N+3}^c. This difference in structure is less outspoken than the one between the two-particle sum rules in two and three dimensions (see Ref. 9). The reason is that both cases here concern an even number of degrees of freedom, which is not true in the two-particle scattering cases. We finally remark that these sum rules can be extended to complex N but this is outside the scope of the present study.

III. THE PLANCK-LARKIN FORM OF THE THIRD CLUSTER INTEGRAL

In this section we study the application of these sum rules to statistical mechanics, in the context of the S-matrix approach which formulates the statistical behavior of a system in terms of the collision processes of the constituent particles.[16]

As is well known,[17] the grand-canonical partition function for a system of N particles having mass m can be expanded in a series in the fugacity with as coefficients the cluster integrals. Assuming the latter exist in the thermodynamic limit, they read in d dimensions, $d=2,3$ (in order to avoid a heavy notation, we do not indicate explicitly, if there is no confusion possible, the dimensional dependence of our quantities)

$$b_1=\lambda^{-d} , \tag{3.1}$$

$$b_2=\frac{2^{d/2}}{2!\lambda^d}\mathrm{Tr}(e^{-\beta h}-e^{-\beta h_0}) , \tag{3.2}$$

$$b_3=\frac{3^{d/2}}{3!\lambda^d}\mathrm{Tr}\left[e^{-\beta H}-e^{-\beta H_0}-\sum_{\alpha=1}^{3}(e^{-\beta H_\alpha}-e^{-\beta H_0})\right] . \tag{3.3}$$

$$\cdots$$

Here λ is the thermal wavelength

$$\lambda=(2\pi\hbar^2\beta/m)^{1/2} , \tag{3.4}$$

and h,h_0 are the total and free two-particle Hamiltonians; H,H_α,H_0 are the three-particle Hamiltonians as defined before. The factors in front of the trace come from the center-of-mass motion. We have assumed Boltzmann statistics. We remark that exchange effects do not introduce anything fundamentally new here but working out their details may be highly nontrivial.

Once we have an explicit form for the b_n, then the grand-canonical participation function and all other thermodynamic properties of the system are determined. The equation of state, e.g., can be obtained as a series in the density of particles ρ. The result is[17]

$$\beta P=\sum_{n=1}^{\infty}a_n\rho^n , \tag{3.5}$$

with P the pressure and where the coefficients a_n, which are the virial coefficients, can be completely written down in terms of the cluster coefficients, viz.,

$$a_1=1,\quad a_2=-b_2b_1^{-2},\quad a_3=4a_2^2-2b_3b_1^{-3},\ \ldots . \tag{3.6}$$

The standard method to write the cluster integrals b_n in terms of scattering quantities is to use the Watson transform, which connects the statistical operator, $\exp(-\beta H)$, with the Green's function $R(z)$, viz.,

$$e^{-\beta H}=-\frac{1}{2\pi i}\oint_C dz\, e^{-\beta z}R(z) , \tag{3.7}$$

where C is again a contour in the complex energy plane around the spectrum of the Hamiltonian. For three-particle scattering, this contour has been specified already in Sec. II. For two-particle scattering, formally the same contour can be taken but the point $-\chi_\alpha^2$ has to be replaced by the origin and the contour lies, of course, in the two-particle energy plane. From (3.2) we then get for $d=2,3$, taking into account explicitly the possibility of zero-energy resonances and/or zero-energy bound states of the two-particle Hamiltonian,

$$b_2(\beta)=2^{d/2-1}\lambda^{-d}\left[\sum_{j=1}^{N_2}e^{\beta\chi_j^2}+D^{(d)}+(2\pi)^{-1}\int_0^\infty dE\, e^{-\beta E}2\,\mathrm{Im}\,\mathrm{Tr}[r(E+i0)-r_0(E+i0)]\right] , \tag{3.8}$$

where the $(-\chi_j^2), j=1,2,\ldots,N_2$, are the two-particle $d=2$ or $d=3$ bound-state positions, $r(E)$ and $r_0(E)$ the total and free $d=2$ or $d=3$ Green's functions, and $D^{(d)}$ the contribution from the zero-energy eigenstates. If there are N_0 of these states, $D^{(3)}$ can have the values $\frac{1}{2}$, N_0, and $(N_0-1)+\frac{1}{2}$ for, respectively, the s-wave-type zero-energy resonance case, the zero-energy bound-state case, and a combination of the latter two (for more details, see Ref. 18). In two dimensions, $D^{(2)}$ can take the values 0, N_0, N_0-1 and N_0 for, respectively, the s-wave-type zero-energy resonance case, the p-wave-type zero-energy resonance case, a combination of the latter two, and the zero-energy bound-state case (for more details, see Ref. 19).

Using the relation between the Green's function difference in (3.8) and the two-particle on-energy-shell S-matrix, $S(E)$, (see, e.g., Ref. 9), the second cluster integral can be written as

$$b_2(\beta)=2^{d/2-1}\lambda^{-d}\left[\sum_{j=1}^{N_2}e^{\beta\chi_j^2}+D^{(d)}+(2\pi)^{-1}\int_0^\infty dE\, e^{-\beta E}\mathrm{Tr}\left[-iS^*(E)\frac{d}{dE}S(E)\right]\right] . \tag{3.9}$$

Equation (3.9) is a generalization of the Beth-Uhlenbeck result[17] to include zero-energy eigenstates and nonspherically symmetric interactions. Indeed, in the case of spherical symmetry we know that the logarithmic derivative of the S matrix is given by the sum of the energy derivatives of the partial-wave phase shifts.

In the same way it is straightforward to derive from (3.3) the following expression for $b_3(\beta)$:

$$b_3(\beta)=\frac{3^{d/2}}{3!\lambda^d}\left[\sum_{j=1}^{N_3}e^{-\beta E_i}+(2\pi)^{-1}\int_{-\chi_\alpha^2}^\infty dE\, e^{-\beta E}2\,\mathrm{Im}\,\mathrm{Tr}R_c(E+i0)\right] , \tag{3.10}$$

where we have assumed that the three-particle bound states do not accumulate at the threshold $-\chi_\alpha^2$. We do not write down the analogue of Eq. (3.9) in this case since there still exists some controversy about the presence of counterterms originating, e.g., from rescattering singularities in the $3-3$ S matrix. For more details we refer to Ref. 20.

In Ref. 8 we have shown for $d=3$ by using higher-order two-particle Levinson theorems, that there is a cancellation in $b_2(\beta)$ [Eq. (3.8)] between the bound-state and scattering contributions. This compensation is rigorously valid on a fully quantum-mechanical level. We refer to Refs. 8 and 11 and the references therein for earlier treatments of this problem. Using this cancellation we have then explained the structure of the two-particle PLPF. As a byproduct we have derived the well-known Wigner-Kirkwood expansion in a novel way.

It is straightforward to generalize these results to two dimensions and furthermore to show that the extra zero-energy contributions $D^{(d)}$ in (3.8) also cancel. We omit all formulas at this point.

As explained in the Introduction the question arises whether a similar program can be carried out for the third (and higher) cluster integral.

Let us look first at $d=3$. Starting from Eq. (3.10) and introducing the notation

$$\tilde{P}_n \equiv (4\pi q)^{-d} \int d\rho\, P_n^c(\rho), \quad d=2,3 \tag{3.11}$$

we can write the continuum part of b_3 as

$$b_3^c(\beta)=\frac{3^{3/2}}{3!\lambda^3}(2\pi)^{-1}\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}[2\,\mathrm{Im\,Tr}R_c(E+i0)-\pi\tilde{P}_2]+\frac{3^{3/2}}{3!\lambda^3}\frac{e^{\beta\chi_\alpha^2}}{2\beta}\tilde{P}_2 \ . \tag{3.12}$$

Here the second term cancels the term we have added in the integrand of the first term. We now rewrite the latter as a total differential in the following way:

$$-\frac{3^{3/2}}{3!\lambda^3}(2\pi)^{-1}\int_{-\chi_\alpha^2}^{\infty} e^{-\beta E} d\left[\int_E^{\infty} dE_1[2\,\mathrm{Im\,Tr}R_c(E_1+i0)-\pi\tilde{P}_2]\right] . \tag{3.13}$$

Partial integration with respect to E and use of the first three-dimensional three-particle sum rule [Eq. (2.14) for $N=0$] to evaluate the surface term gives, then,

$$b_3^c(\beta)=\frac{3^{3/2}}{3!\lambda^3}\left[(2\pi)^{-1}e^{\beta\chi_\alpha^2}[-2\pi N_3-(2\pi/6)\tilde{P}_3]+\frac{e^{\beta\chi_\alpha^2}}{2\beta}\tilde{P}_2\right.$$
$$\left.-(2\pi)^{-1}\beta\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}\int_E^{\infty} dE_1[2\,\mathrm{Im\,Tr}R_c(E_1+i0)-\pi\tilde{P}_2]\right] . \tag{3.14}$$

The last term in (3.14) can again be written as a complete differential. Partial integration and some further algebraic manipulations lead to the following expression for this term:

$$-\frac{3^{3/2}}{3!\lambda^3}(2\pi)^{-1}\beta e^{\beta\chi_\alpha^2}\left[\chi_\alpha^2\int_{-\chi_\alpha^2}^{\infty} dE[2\,\mathrm{Im\,Tr}R_c(E+i0)-\pi\tilde{P}_2]+\int_{-\chi_\alpha^2}^{\infty} dE\, E[2\,\mathrm{Im\,Tr}R_c(E+i0)-\pi\tilde{P}_2]\right]$$
$$+\frac{3^{3/2}}{3!\lambda^3}(2\pi)^{-1}\beta^2\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}\int_E^{\infty} dE_2\int_{E_2}^{\infty} dE_1[2\,\mathrm{Im\,Tr}R_c(E_1+i0)-\pi\tilde{P}_2] . \tag{3.15}$$

We now employ the three-particle sum rules (2.14) for $N=0$ and $N=1$ to arrive at the following formula for b_3:

$$b_3(\beta)=\frac{3^{3/2}}{3!\lambda^3}\left[\sum_{j=1}^{N_3} e^{-\beta E_j}+e^{\beta\chi_\alpha^2}(1-\beta\chi_\alpha^2)(-N_3-\tilde{P}_3/6)+e^{\beta\chi_\alpha^2}\left[\sum_j \beta E_j+\beta\tilde{P}_4/24\right]+\frac{e^{\beta\chi_\alpha^2}}{2\beta}\tilde{P}_2\right.$$
$$\left.+(2\pi)^{-1}\beta^2\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}\int_E^{\infty} dE_2\int_{E_2}^{\infty} dE_1[2\,\mathrm{Im\,Tr}R_c(E_1+i0)-\pi\tilde{P}_2]\right] . \tag{3.16}$$

It is clear that this process may again be repeated. We write down the result after one more step,

$$b_3^{(3)}(\beta)=\frac{3^{3/2}}{3!\lambda^3}\left[\sum_{j=1}^{N_3} e^{-\beta E_j}+e^{\beta\chi_\alpha^2}(1-\beta\chi_\alpha^2+\tfrac{1}{2}\beta^2\chi_\alpha^4)(-N_3-\tilde{P}_3/6)+e^{\beta\chi_\alpha^2}(1-\beta\chi_\alpha^2)\left[\sum_j \beta E_j+\beta\tilde{P}_4/24\right]\right.$$
$$+e^{\beta\chi_\alpha^2}\left[-\tfrac{1}{2}\sum_j \beta^2 E_j^2-\beta^2\tilde{P}_5/120\right]+\frac{e^{\beta\chi_\alpha^2}}{2\beta}\tilde{P}_2$$
$$\left.-(2\pi)^{-1}\beta^3\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}\int_E^{\infty} dE_3\int_{E_3}^{\infty} dE_2\int_{E_2}^{\infty} dE_1[2\,\mathrm{Im\,Tr}R_c(E_1+i0)-\pi\tilde{P}_2]\right] , \tag{3.17}$$

where the superscript (3) now indicates explicitly that we are working in $d=3$ and where $\tilde{P}_n$ is given by (3.11) with $d=3$.

Before discussing these formulas we write down the equivalent of (3.17) for $d=2$, obtained by the same procedure starting from (3.10) and using now the sum rules (2.20)

$$b_3^{(2)}(\beta)=\frac{1}{2\lambda^2}\left[\sum_{j=1}^{N_3} e^{-\beta E_j}+e^{\beta\chi_\alpha^2}(1-\beta\chi_\alpha^2+\tfrac{1}{2}\beta^2\chi_\alpha^4)(-N_3+\tilde{P}_2/2)+e^{\beta\chi_\alpha^2}(1-\beta\chi_\alpha^2)\left[\sum_j \beta E_j-\beta\tilde{P}_3/6\right]\right.$$
$$+e^{\beta\chi_\alpha^2}\left[-\tfrac{1}{2}\sum_j \beta^2 E_j^2+\beta^2\tilde{P}_4/24\right]$$
$$\left.-(2\pi)^{-1}\beta^3\int_{-\chi_\alpha^2}^{\infty} dE\, e^{-\beta E}\int_E^{\infty} dE_3\int_{E_3}^{\infty} dE_2\int_{E_2}^{\infty} dE_1[2\,\mathrm{Im}\,\mathrm{Tr}R_c(E_1+i0)]\right], \tag{3.18}$$

where $\tilde{P}_n$ is again given by (3.11) but with $d=2$.

We clearly see the pattern of cancellation between bound-state and scattering contributions in (3.17) and (3.18). It is more complicated than the one for the second cluster integral $b_2(\beta)$ (see, e.g., Refs. 8 and 9). This is due to the presence of the threshold factor $\exp(\beta\chi_\alpha^2)$, which is there because we have included three-particle processes such as rearrangement and breakup. If this factor is absent ($\chi_\alpha^2=0$), then the cancellation is like in the case of $b_2(\beta)$.

These cancellations make the existence of an effective bound-state sum or Planck-Larkin structure apparent. If we consider the first three terms of (3.17) or (3.18), and keep all contributions up to order β coming from the bound states, we get

$$b_3^{\mathrm{Pl}}(\beta)=\frac{3^{d/2}}{3!\lambda^d}\left[\sum_{j=1}^{N_3} e^{-\beta E_j}-N_3+\sum_j \beta E_j\right]. \tag{3.19}$$

In the case of a multi-electron hydrogen partition function, the existence of such a structure has been discussed by Rogers[11] in a semiclassical context. Here we have used the full quantum-mechanical higher-order sum rules [e.g., (2.14) for $N=0,1$ in $d=3$], valid for potentials that are smooth enough to ensure the existence of $\tilde{P}_2$ to $\tilde{P}_n$ ($n=4$ in $d=3$), to obtain (3.19).

It is clear that this compensation is not affected by letting $(-\chi_\alpha^2)$ become very small, meaning the system has very low-energy bound states. If, in $d=3$, we take $(-\chi_\alpha^2)\to 0_-$ such that a two-particle bound state exists at zero energy, then the number of three-particle bound states N_3 will become infinite (i.e., the Efimov effect, which does not exist for $d=2$). Even in this limiting point, the sum rule (2.14) stays valid formally—both sides are infinite—and the manipulations leading to (3.17)–(3.19) go through. So there will be a cancellation between bound-state and scattering contributions at the Efimov point, implying that the third cluster integral stays finite also there. This has been shown first in a model calculation by Hoogeveen and Tjon.[12]

Another nice feature of (3.17)–(3.19) is that these formulas show explicitly, on the basis of Levinson's theorem, that the third cluster integral does not change discontinuously when a new three-particle bound state is formed by changing potential strength. This is necessary on physical grounds: any discontinuity would be reflected in the thermodynamic properties of the system [cf., e.g., Eqs. (3.5) and (3.6)]. In the case of the second cluster integral it has been shown recently[21] that this continuity in the coupling constant can be used reversely to infer the form of Levinson's theorem. For the present situation of three-particle scattering this behavior in the (two-particle) coupling constant is much more difficult to analyze.[22] Nevertheless, it would be interesting to study whether a three-particle Levinson theorem can be obtained in an analogous way from the third cluster integral.

It is clear that, in principle, the methods used in this section can be applied to look at the structure of the higher cluster coefficients. The practical realization of this study, however (four-particle sum rules, etc.) will be more complicated.

Finally, comparing (3.17) and (3.18) we see already that in three dimensions the term $[(2\beta)^{-1}\exp(\beta\chi_\alpha^2)\tilde{P}_2]$ will not be compensated for by repeating the procedure outlined before to obtain these formulas. This will be discussed further in Sec. IV.

IV. WIGNER-KIRKWOOD-TYPE-EXPANSION FOR THE THIRD VIRIAL COEFFICIENT

If one keeps repeating the procedure used in Sec. III to derive (3.17) and (3.18), one finally arrives at the following expansions for the third cluster integral in three and two dimensions:

$$b_3^{(3)}(\beta)=\frac{3^{3/2}}{3!\lambda^3}\frac{1}{(4\pi q)^3}\left[\frac{e^{\beta\chi_\alpha^2}}{2\beta}\int d^6\rho\, P_2^c(\rho)\right.$$
$$\left.+\sum_{n=3}^{\infty}\frac{(-1)^n}{n!}\beta^{n-3}\int d^6\rho\, P_n^c(\rho)\right], \tag{4.1}$$

$$b_3^{(2)}(\beta)=\frac{1}{2\lambda^2}\frac{1}{(4\pi q)^2}\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}\beta^{n-2}\int d^4\rho\, P_n^c(\rho). \tag{4.2}$$

As remarked already before, the three-dimensional result contains a term with factor $\exp(\beta\chi_\alpha^2)$. This gives an explicit dependence of $b_3^{(3)}(\beta)$ on χ_α^2, the two-particle threshold, originating from the correction term in the

sum rules (2.14). For $\chi_\alpha^2=0$ this term can be simply absorbed in the sum over n in (4.1).

At this point we recall that in Ref. 8 we have obtained in an analogous but simpler way, as a byproduct of our study of the two-particle PLPF, the well-known Wigner-Kirkwood expansion for the second virial coefficient. The method used there can be generalized in a straightforward way to two dimensions by using the corresponding sum rules derived in Ref. 9. We only mention the final result here

$$a_2^{(d)}(\beta)=-\lambda^{2d}\frac{1}{2}\left[\frac{2m}{\hbar^2}\right]^d(4\pi)^{-d}\times\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\beta^{n-d}\int d^dx\,P_n(\mathbf{x})$$
$$=-\tfrac{1}{2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\beta^n\int d^dx\,P_n(\mathbf{x}),\quad d=2,3\ , \tag{4.3}$$

where the $P_n(\mathbf{x})$ are polynomials in the potential and its derivatives, that can be found, e.g., in Ref. 14. For completeness we present the first few,

$$P_1(\mathbf{x})=V(\mathbf{x})\ ,$$
$$P_2(\mathbf{x})=V^2(\mathbf{x})-\left[\frac{\hbar^2}{2\mu}\right]\tfrac{1}{3}\Delta V(\mathbf{x})\ , \tag{4.4}$$
$$P_3(\mathbf{x})=V^3(\mathbf{x})-\left[\frac{\hbar^2}{2\mu}\right]\{V(\mathbf{x})\Delta V(\mathbf{x})+\tfrac{1}{2}[\nabla V(\mathbf{x})]^2\}+\left[\frac{\hbar^2}{2\mu}\right]^2\tfrac{1}{10}\Delta^2V(\mathbf{x})\ ,$$

with μ the two-particle reduced mass and ∇ the d-dimensional nabla operator. The potential and a number of its derivatives, the number depending on n, are supposed to be smooth enough such that the x-integrals in (4.3) exist.

We now have all the necessary information to derive a Wigner-Kirkwood expansion for the third virial coefficient starting from Eq. (3.6), i.e.,

$$a_3=4a_2^2-2b_3b_1^{-3}\ ,$$

For $d=3$ we obtain, using (4.1) and (4.3),

$$a_3=\sum_{n=2}^{\infty}(-1)^n\beta^n\sum_{l=1}^{n-1}\frac{1}{(n-l)!l!}\int d^3x\,P_{n-l}(\mathbf{x})\int d^3x'\,P_l(\mathbf{x}')$$
$$-\tfrac{1}{3}\left[\tfrac{1}{2}\beta^2e^{\beta\chi_\alpha^2}\int d^6\rho\,P_2^c(\boldsymbol{\rho})+\sum_{n=3}^{\infty}\frac{(-1)^n}{n!}\beta^n\int d^6\rho\,P_n^c(\boldsymbol{\rho})\right]\ , \tag{4.5}$$

where the P_n^c are given by (2.11), (2.15), and (2.16). It is now straightforward to check that after expanding $\exp(\beta\chi_\alpha^2)$ in β and using the expressions for P_1 and P_2^c, the terms of order β^2 in (4.5) cancel. So the final result for the third virial coefficient in three dimensions reads

$$a_3^{(3)}(\beta)=\sum_{n=3}^{\infty}(-1)^n\beta^n\sum_{l=1}^{n-1}\frac{1}{(n-l)!l!}\int d^3x\,P_{n-l}(\mathbf{x})\int d^3x'\,P_l(\mathbf{x}')$$
$$-\tfrac{1}{3}\sum_{n=3}^{\infty}\beta^n\left[\frac{(\chi_\alpha^2)^{n-2}}{(n-2)!}\int d^6\rho\,P_2^c(\boldsymbol{\rho})+\frac{(-1)^n}{n!}\int d^6\rho\,P_n^c(\boldsymbol{\rho})\right]\ . \tag{4.6}$$

This is the Wigner-Kirkwood (i.e., high-temperature) expansion for the third virial coefficient of a Boltzmann gas of particles of mass m. No approximations have been made and all three-particle processes such as rearrangement scattering and breakup have been taken into account. As far as we know, this result is new. We remark that in the case $\chi_\alpha^2=0$ there may be further cancellation of terms in (4.6) depending on the specific model discussed. E.g., Hoogeveen and Tjon[12] find in their model calculation of a gas mixture of light and heavy particles, assuming the interaction between the heavy and light particles to be local, that $a_3^{(3)}(\beta)$ vanishes in the classical limit and that the leading order in the quantum correction becomes β^6.

For $d=2$ a similar discussion using (4.2) and (4.3) leads to the following Wigner-Kirkwood expansion:

$$a_3^{(2)}(\beta)=\sum_{n=3}^{\infty}(-1)^n\beta^n\sum_{l=1}^{n-1}\frac{1}{(n-l)!l!}\int d^2x\,P_{n-l}(\mathbf{x})\int d^2x'\,P_l(\mathbf{x}')-\tfrac{1}{3}\sum_{n=3}^{\infty}\frac{(-1)^n}{n!}\beta^n\int d^4\rho\,P_n^c(\boldsymbol{\rho})\ . \tag{4.7}$$

Both the expansions (4.6) and (4.7) have as leading order β^3. Both the second virial coefficients (4.3) start already with order β, but the first quantum correction arises in the term β^3.

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