«ФИЗИКА ЭЛЕМЕНТАРНЫХ ЧАСТИЦ И АТОМНОГО ЯДРА»
2000, ТОМ 31, ВЫП. 7Б

УДК 536.75, 538.9

HYPERSPHERICAL ADIABATIC FORMALISM OF THE BOLTZMANN THIRD VIRIAL

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First, we show that, if there are no bound states, we can express the q.m. third cluster — involving 3 and fewer particles in Statistical Mechanics — as a formula involving adiabatic eigenphase shifts. This is for Boltzmann statistics.

From this q.m. formulation, in the case of purely repulsive forces, we recover, as $\hbar$ goes to 0, the classical expressions for the cluster.

We then discuss difficulties which arise in the presence of 2-body bound states and present a tentative formula involving eigenphase shifts and the 2- and 3-body bound state energies. We emphasize that important difficulties have not been resolved.

STATISTICAL MECHANICS

In equilibrium Statistical Mechanics ALL wisdom derives from the partition function! Here, we need the logarithm of the Grand Partition function $\mathcal{Q}$:

$$\begin{aligned}\ln \mathcal{Q} &= z\ Tr(e^{-\beta T_1}) \\ &+ z^2\,[Tr(e^{-\beta H_2}) - \frac{1}{2}(Tr(e^{-\beta T_1}))^2] \\ &+ z^3\,[Tr(e^{-\beta H_3}) - Tr(e^{-\beta T_1})Tr(e^{-\beta H_2}) + \frac{1}{3}(Tr(e^{-\beta T_1})^3] \\ &+ \cdots\end{aligned}$$

which, when divided by V, gives coefficients which are independent of the volume, when the latter becomes large; we call them b_l. The fugacity z equals $\exp(\mu/\kappa T)$, where μ is the Gibbs function per particle, κ is Boltzmann's constant and T is the temperature; $\beta = 1/\kappa T$. We can then write for the pressure and the density

$$p/\kappa T = (1/V)\ln \mathcal{Q} = \sum_l b_l\, z^l$$

$$N/V = \rho = \sum_l l\, b_l\, z^l.$$

The fugacity can then be eliminated to give the pressure in terms of the density.

$$p/kT = \rho + \cdots$$

The coefficients of the second and higher powers are called the virial coefficients.

Crucial Step. For this work we extract the Boltzmann part of the traces: we write

$$Tr(e^{-\beta H_n}) = \frac{1}{n!}\,\mathrm{Trace}^B(e^{-\beta H_n}) + \text{Exchange Terms.}$$

We can then write for the Boltzmann b_3:

$$b_3 = (3!V)^{-1}\,\mathrm{Trace}^B[(e^{-\beta H_3} - e^{-\beta T_3}) - 3\,(e^{-\beta(H_2+T_1)} - e^{-\beta T_3})],$$

where I have made use of the Boltzmann statistics to express the answer in terms of 3-body traces.

ADIABATIC PRELIMINARIES

For 3 particles of equal masses, in three dimensions, we first introduce centre-of-mass and Jacobi coordinates. We define

$$\vec{\eta} = \left(\frac{1}{2}\right)^{1/2}(\vec{r}_1 - \vec{r}_2)\,,\; \vec{\xi} = \left(\frac{2}{3}\right)^{1/2}\left(\frac{\vec{r}_1 + \vec{r}_2}{2} - \vec{r}_3\right),\; \vec{R} = \frac{1}{3}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3)$$

where, of course, the $\vec{r}_i$ give us the locations of the 3 particles. This is a canonical transformation and insures that in the kinetic energy there are no cross terms.

The variables $\vec{\xi}$ and $\vec{\eta}$ are involved separately in the Laplacians and we may consider them as acting in different spaces. We introduce a higher dimensional vector $\vec{\rho} = \begin{pmatrix} \vec{\xi} \\ \vec{\eta} \end{pmatrix}$ and express it in a hyperspherical coordinate system (ρ and the set of angles Ω). If we factor a term of $\rho^{5/2}$ from the solution of the relative Schrödinger equation, i.e., we let $\psi = \phi/\rho^{5/2}$, we are led to:

$$\left[-\frac{\partial^2}{\partial\rho^2} + H_\rho - \frac{2mE}{\hbar^2}\right]\phi(\rho,\Omega) = 0,$$

where

$$H_\rho = -\frac{1}{\rho^2}\left[\nabla^2_\Omega - \frac{15}{4}\right] + \frac{2m}{\hbar^2}V(\rho,\Omega)$$

and m is the mass of each particle, E is the relative energy in the centre of mass. ∇^2_Ω is the purely angular part of the Laplacian. We now introduce the adiabatic basis, which consists of the eigenfunctions of part of the Hamiltonian: the angular part of the kinetic energy and the potential.

$$H_\rho B_\ell(\rho,\Omega) = \Lambda_\ell(\rho) B_\ell(\rho,\Omega),$$

where ℓ enumerates the solutions.

Using this adiabatic basis, we can now rewrite the Schrödinger equation as a system of coupled ordinary differential equations. We write

$$\phi(\rho,\Omega) = \sum_{\ell'} B_{\ell'}(\rho,\Omega)\tilde{\phi}_{\ell'}(\rho)$$

and obtain the set of coupled equations

$$\begin{aligned}(\frac{d^2}{d\rho^2} - \Lambda_\ell(\rho) \quad &+ \quad k^2)\tilde{\phi}_\ell(\rho) + 2\sum_{\ell'} C_{\ell,\ell'}\,\frac{d}{d\rho}\tilde{\phi}_{\ell'}(\rho) \\ &+ \quad \sum_{\ell'} D_{\ell,\ell'}\,\tilde{\phi}_{\ell'}(\rho) = 0,\end{aligned}$$

where k^2 is the relative energy multiplied by $2m/\hbar^2$ and we defined:

$$\begin{aligned}C_{\ell,\ell'}(\rho) \quad &= \quad \int d\Omega\, B^*_\ell(\Omega,\rho)\frac{\partial}{\partial\rho}B_{\ell'}(\Omega,\rho), \\ D_{\ell,\ell'}(\rho) \quad &= \quad \int d\Omega\, B^*_\ell(\Omega,\rho)\frac{\partial^2}{\partial\rho^2}B_{\ell'}(\Omega,\rho).\end{aligned}$$

We note that

$$D_{\ell,\ell'} = \frac{d}{d\rho}\left(C_{\ell,\ell'}\right) + \left(C^2\right)_{\ell,\ell'}.$$

THE PHASE SHIFT FORMULA

When there are no bound states, we may write

$$Tr^B(e^{-\beta H_3}) = \int d\vec{\rho} \int dk \sum_i \psi^i(k,\vec{\rho})(\psi^i(k,\vec{\rho}))^*\; e^{-\beta\left(\frac{\hbar^2}{2m}k^2\right)},$$

where we have introduced a complete set of continuum eigenfunctions. Expanding in the adiabatic basis, we obtain

$$Tr^B(e^{-\beta H_3}) = \int d\rho \int dk \sum_{i,\ell} |\tilde{\phi}^i_\ell(k,\rho)|^2\; e^{-\beta(\frac{\hbar^2}{2m}k^2)},$$

where we note that we have integrated over the angles and taken advantage of the orthogonality of our B_l's. We integrate from 0 to ∞.

We now return to our expression for b_3 and proceed as above, but drop the tildas, to obtain:

$$\frac{3^{1/2}}{2\lambda_T^3}\int dk\, e^{-\beta E_k}\int d\rho \sum_{i,\ell}[(|\phi_\ell^i|^2 - |\phi_{\ell,0}^i|^2) - 3(|\bar{\phi}_\ell^i|^2 - |\bar{\phi}_{\ell,0}^i|^2)],$$

where we have evaluated the trace corresponding to the centre of mass. The amplitudes ϕ_ℓ^i correspond to H_3, $\bar{\phi}_\ell^i$ to H_2+T_1 and amplitudes with a zero belong to the free particles. The thermal wavelength λ_T is defined as $h/\sqrt{2\pi m\kappa T}$.
We now make use of a trick to evaluate the ρ integrals. We first write

$$\int_0^{\rho_{\max}} \sum_\ell |\phi_\ell^i(k,\rho)|^2\, d\rho = \lim_{k'\to k}\int_0^{\rho_{\max}} \sum_\ell \phi_\ell^i(k,\rho)\phi_\ell^i(k',\rho)\, d\rho$$

and then, and there is the trick,

$$\int_0^{\rho_{\max}} \sum_\ell (\;\phi_\ell^i(k,\rho)\;\; \phi_\ell^i(k',\rho))d\rho =$$
$$\frac{1}{k^2-(k')^2}\sum_\ell [\;\phi_\ell^i(k,\rho)\;\; \frac{d}{d\rho}\phi_\ell^i(k',\rho) - \phi_\ell^i(k',\rho)\frac{d}{d\rho}\phi_\ell^i(k,\rho)],$$

evaluated at $\rho = \rho_{\max}$.

That is, our identity is:

$$\sum_\ell \frac{d}{d\rho}\left[\phi_\ell(k')\frac{d}{d\rho}\phi_\ell(k) - \phi_\ell(k)\frac{d}{d\rho}\phi_\ell(k')\right]$$
$$+\left(k^2-(k')^2\right)\sum_\ell \phi_\ell(k)\;\phi_\ell(k')$$
$$+2\sum_{\ell,\ell'}\frac{d}{d\rho}\left[\phi_\ell(k')\;C_{\ell,\ell'}\;\phi_{\ell'}(k)\right] = 0$$

and we integrate with respect to ρ. Using then the fact that ϕ goes to zero, as ρ itself goes to zero, and that C decreases fast enough for ρ large, we are left with the expression displayed earlier (that of our «trick»).

We now put in the asymptotic form of our solutions, oscillatory solutions valid for $\rho_{\max}$ large, and use l'Hospital's rule to take the limit as $k' \to k$. The solutions are:

$$\phi_\ell^i \to (k\rho)^{1/2}\mathcal{C}_{\ell,i}\,[\cos\delta_i\; J_{K+2}(k\rho) - \sin\delta_i\; N_{K+2}(k\rho)],$$

where the order K is one of the quantities specified by ℓ. Inserting this into our integrals we find that

$$\sum_\ell \int_0^{\rho_{\max}} |\phi_\ell^i(k)|^2 \, d\rho \to \frac{1}{\pi}\frac{d}{dk}\delta^i(k) + \frac{1}{\pi}\rho_{\max} \, + \, \text{osc. terms}$$

and, thus, that

$$\int_0^{\rho_{\max}} (|\phi_\ell^i(k)|^2 - |\phi_{\ell,0}^i(k)|^2) \, d\rho \to \frac{1}{\pi}\frac{d}{dk}\delta^i(k) \, + \, \text{osc. terms.}$$

We let $\rho_{\max}$ go to infinity, and the oscillating terms — of the form $\sin(2k\rho_{\max} + \cdots)$ — will not contribute to the subsequent integration over k. A partial integration now gives us our basic formula

$$b_3^{\text{Boltz}} = \frac{3^{1/2}}{(2\pi)^2\lambda_T}\int_0^\infty dk \, k \, G(k) \, e^{-\beta\frac{\hbar^2}{2m}k^2},$$

where

$$G(k) = \sum_i [\delta_i(k) - 3\,\bar{\delta}_i(k)].$$

The first δ arises from comparing three interacting particles with three free particles. The second $\bar{\delta}$ arises when a 3-body system, where only two particles are interacting (one particle being a spectator), is compared to three free particles.

CLASSICAL LIMIT

The idea behind our WKB treatment of our equations, is to argue that when the potentials change slowly — within oscillations of the solutions — then the adiabatic eigenfunctions will also change slowly and we can neglect their derivatives. Thus we will obtain **uncoupled** equations with effective potentials (the eigenpotentials $\Lambda_\ell(\rho)$). We then proceed with these in a more or less conventional WKB fashion. Let us assume, here, one turning point ρ_0.

The phases can now be obtained by considering simplified forms of the asymptotic solutions for the $\phi's$. Let us denote them as ϕ_ν. The phases will then be

$$\delta_\nu \sim (K+2)\frac{\pi}{2} - k\rho_0 + \int_{\rho_0}^\infty \left[\sqrt{k^2 - \Lambda_\nu - \frac{1}{4\rho^2}} - k\right] d\rho.$$

Inserting our expression for δ_ν into $\int_0^\infty dk\, k\, \delta_\nu(k)\, \exp\left(-\lambda_T^2 k^2/4\pi\right)$ and interchanging the order of integration (ρ and k) we obtain:

$$\frac{2(\pi^2)}{\lambda_T^3}\int_0^\infty d\rho \left\{ \exp\left[-\frac{\lambda_T^2}{4\pi}(\Lambda_\nu + \frac{1}{4\rho^2})\right] - \exp\left[-\frac{\lambda_T^2}{4\pi}\frac{(K+2)^2}{\rho^2}\right]\right\}.$$

Summing now over ν, we can rewrite the exponentials as traces:

$$\sum_\nu \{ \exp\left[-\frac{\lambda_T^2}{4\pi}\left(\Lambda_\nu + \frac{1}{4\rho^2}\right)\right] - \exp\left[-\frac{\lambda_T^2}{4\pi}\frac{(K+2)^2}{\rho^2}\right]\}$$
$$= \mathrm{Trace}^R \left\{ \exp\left[-\frac{\lambda_T^2}{4\pi}\left(\Lambda(\rho) + \frac{1}{4\rho^2}\right)\right] - \exp\left[-\frac{\lambda_T^2}{4\pi}\frac{\mathcal{K}^2 + \frac{1}{4}}{\rho^2}\right]\right\},$$

where Λ is the operator (matrix) which yields the diagonal elements Λ_ν and $\mathcal{K}^2$ the operator which yields the eigenvalue when the interaction is turned off (and therefore takes on the diagonal values $(K+2)^2 - \frac{1}{4}$, associated with the hyperspherical harmonic of order K). The trace is restricted so as not to involve ρ.

In another key step, we switch to a hyperspherical basis. We note that Λ is related to $(2m/\hbar^2)\, V + \mathcal{K}^2/\rho^2$ by a similarity transformation and an orthogonal matrix U. Substituting in the trace, we lose the U and obtain

$$\mathrm{Tr}^R \left[\exp\left(-\beta V - \frac{\lambda_T^2}{4\pi}\frac{\mathcal{K}^2 + \frac{1}{4}}{\rho^2}\right) - \exp(-\frac{\lambda_T^2}{4\pi}\frac{\mathcal{K}^2 + \frac{1}{4}}{\rho^2})\right].$$

We write the exponential as a product of 2 exponentials, disregarding higher order terms in $\hbar$. Introducing eigenkets and eigenbras which depend on the hyperspherical angles, we write the trace as:

$$\int d\Omega < \Omega| \exp(-\frac{\lambda_T^2}{4\pi}\frac{\mathcal{K}^2 + \frac{1}{4}}{\rho^2})|\Omega > \{\exp[-\beta V(\vec{\rho})] - 1\}.$$

The matrix element above can be evaluated and, to leading order in a Euler McLaurin expansion, yields ρ^5/λ_T^5. For the phase shifts of type δ_ν, associated with the fully interacting 3 particles, V equals $V(12) + V(13) + V(23)$ and we obtain as its contribution to b_3^{Boltz}:

$$\frac{3^{1/2}}{2\lambda_T^9}\int d\vec{\xi}\, d\vec{\eta}\, (\exp[-\beta(V(12)+V(13)+V(23))]-1).$$

The expression above, derived solely from the contribution of the δ's, diverges for infinite volume. However, including the terms in $\bar{\delta}$, associated with the pairs 12, 13 and 23, provides a convergent answer. The complete result for b_3^{Boltz} divided by b_1^3, where $b_1 = \lambda_T$, equals

$$\frac{1}{3!V}\int d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, \{\exp[-\beta(V(12)+V(13)+V(23))]$$
$$- \exp[-\beta V(12)] - \exp[-\beta V(13)] - \exp[-\beta V(23)] + 2\},$$

where I have integrated over $\vec{R}$ the center of mass coordinate, divided by V, and changed to the coordinates $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$. The result is the classical expression with all the correct factors.

BOUND STATES

If there are bound states, the major change in the eigenpotentials is that for some of these potentials, instead of going to zero at large distances (large ρ), there appears a negative «plateau», i.e., the eigenpotential (up to some contribution in $1/\rho^2$), becomes flat and negative. This is the indication that asymptotically the physical system consists of a 2-body bound state and a free particle. The eigenpotential may also «support» one or more 3-body bound states.
The eigenfunction expansion of the trace associated with H_3, will read:

$$\sum_m \exp(-\beta E_{3,m}) + \sum_i \int_0^\infty dk \int d\vec{\rho}\, \psi^i(k,\vec{\rho})\, (\psi^i(k,\vec{\rho}))^* \ \exp\left\{-\beta\left(\frac{\hbar^2}{2m}k^2\right)\right\}$$
$$+ \sum_i \int_0^{q_i} dq \int d\vec{\rho}\, \psi^i(q,\vec{\rho})\, (\psi^i(q,\vec{\rho}))^* \ \exp\left\{-\beta\left(\frac{\hbar^2}{2m}q^2 - \epsilon_{2,i}\right)\right\}.$$

The q's are defined by $k^2 = q^2 - \epsilon_{2,i}$, where $\epsilon_{2,i}$ is the binding energy of the corresponding bound state. The limit q_i equals $\sqrt{\frac{2m}{\hbar^2}\epsilon_{2,i}}$. The new continuum term represents solutions which are still oscillatory for negative energies (above that of the respective bound states).

Assume, now, that we have 1 bound state, and introduce amplitudes. The asymptotic behaviour will be as follows.
For $E > 0$.

$$\phi^i_\ell(\rho) \to (k\rho)^{1/2}\mathcal{C}_{\ell,i}\,[\cos\delta_i\, J_{K_\ell+2}(k\rho) - \sin\delta_i\, N_{K_\ell+2}(k\rho)]$$

$$\phi^i_{\ell_0}(\rho) \to (k\rho)^{1/2}\mathcal{C}_{\ell_0,i}\,[\cos\delta_i\, J_{K_{\ell_0}+2}(q\rho) - \sin\delta_i\, N_{K_{\ell_0}+2}(q\rho)].$$

Using our procedure as before we obtain for the integral over ρ:

$$\frac{1}{\pi}\frac{d}{dk}\delta_i + \frac{\rho_{\max}}{\pi}\left(\sum_{\ell\neq\ell_0}|\mathcal{C}_{\ell,i}|^2 + |\mathcal{C}_{\ell_0,i}|^2\frac{k}{q}\right).$$

For $E < 0$,

$$\phi^i_{\ell_0}(\rho) \to (q\rho)^{1/2}[\cos\delta_i\, J_{K_{\ell_0}+2}(q\rho) - \sin\delta_i\, N_{K_{\ell_0}+2}(q\rho)]$$

which then yields

$$\frac{1}{\pi}\frac{d}{dk}\delta_i + \frac{\rho_{\max}}{\pi}.$$

The problem is that I can no longer eliminate the $\rho_{\max}$ term by subtracting the contribution of the free particle term, i.e., using the $\rho_{\max}$ from T_3 to cancel the $\rho_{\max}$ from H_3. **All is not lost** however, as we saw (for example in the terms arising in the classical limit) that all the terms of the cluster (b_3) are needed to obtain a volume-independent and convergent result. The obvious terms to examine are the ones associated with $H_2 + T_1$, which also have amplitudes that correspond to (2-body) bound states. I have not been able, to date, to prove that all the coefficients are such that the final coefficient of $\rho_{\max}$ is zero.

If we were ... to assume that the terms in $\rho_{\max}$ **do** indeed cancel, then we can write the following formula for the complete trace.

$$\begin{aligned}
&\mathrm{Trace}^B[(e^{-\beta H_3} - e^{-\beta T_3}) - 3\,(e^{-\beta(H_2+T_1)} - e^{-\beta T_3})] \\
&= \sum_m e^{-\beta E_{3,m}} + \frac{1}{\pi}\sum_i \int_0^\infty dk \frac{d}{dk}[\delta_i(k) - 3\bar{\delta}_i(k)] e^{-\beta(\frac{\hbar^2}{2m}k^2)} \\
&\qquad\qquad + \frac{1}{\pi}\sum_i e^{\beta\epsilon_i} \int_0^{q_i} dq \frac{d}{dq}[\delta_i(q) - 3\bar{\delta}_i(q)] e^{-\beta(\frac{\hbar^2}{2m}q^2)}.
\end{aligned}$$