Generating functional of one-component classical systems in the ergodic approximation

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Abstract. An exact integral representation of the generating functional of a many-body classical system with a factorized structure of the integrand over the coordinates of the particles is obtained. One-particle factors in this expression are calculated using Weyl’s ergodic theorem. The radial distribution function of systems with a double Yukawa interatomic potential is calculated and investigated.

1. Introduction

The generating functional of a many-particle system is the partition function of this system in the presence of an arbitrary external field. The method of generating functional is an effective method for studying of multiparticle systems. In particular, differentiating the generating functional with respect to the external field or interatomic potentials allows one to calculate the correlation functions, lower the symmetry of the Hamiltonian of the system to realize the concept of quasiaverages in statistical mechanics, etc.

Consider the classical system of \( N \) identical particles that are in a box of volume \( V \) and interacting with each other through some pair potential \( v(r) \). The Hamiltonian of the particles of this system, interacting with each other and with a time-independent external field \( \varphi(R) \), is given by the expression

\[
H(p,q) = K(p) + W(q) = \sum_{s=1}^{N} \frac{p_s^2}{2m} + \frac{1}{2} \sum_{s<s'} v(R_s - R_{s'}) + \sum_{s=1}^{N} \varphi(R_s),
\]

(1)

where \( R_s \) is the radius vector of the position of the \( s \)-th particle. The microscopic particle density \( \rho(q) \) is defined by the expression

\[
\rho(q) = \sum_{s=1}^{N} \delta(q - R_s),
\]

(2)

where \( \delta(q) \) is the Dirac delta function. The Hamiltonian of the system in terms of microscopic density has the form

\[
H(p,q) = K(p) + \frac{1}{2} \int n(r) v(r - r') n(r') \, dr \, dr' + \int \int \varphi(r) n(r) \, dr - \frac{N}{2} \varphi(0).
\]

The last term \( -N\varphi(0)/2 \) compensates for the “extra” term corresponding to \( s = s' \) in (1). Thus, the Hamiltonian of the system is a functional of microscopic density, as well as of the interatomic potential \( v(r) \) and the external field \( \varphi(r) \). The canonical generating functional is also the functional of the
interatomic potential and the external field:

\[ Z[n] = e^{\frac{BN}{\pi A}} \int \exp\left\{-\beta \left[ K(p) + \int \varphi(r) \, n(r) \, dr \right]\right\} \times \exp\left\{-\beta \frac{1}{2} \int \nu(r - r') \, n(r) \, n(r') \, dr \, dr'ight\} d\Gamma. \]  

Here \( \beta = 1/T \), \( T \) is absolute temperature in energy units.

After integration over the momentum variables, the generating functional has the form:

\[ Z[\varphi(r)] = \nu^N e^{\frac{BN}{N_\lambda^2N(0)}} \int (\nu) \left( \prod_{k=1}^{N_\lambda^2} \frac{d^3r_k}{v} \right) \exp(-\beta \int \varphi(r) \, n(r) \, dr) \times \exp\left(-\frac{\beta}{2} \int \nu(r - r') \, n(r) \, n(r') \, dr \, dr'\right). \]  

where \( \lambda = \hbar/\sqrt{2\pi\beta/m} \) is de Broglie thermal wavelength.

The average local density \( \langle n(r) \rangle \) can be found from the generating functional using functional differentiation with respect to the external field \([1, 2]\]

\[ \frac{\delta \ln Z}{\delta \varphi(r)} = -\beta \langle n(r) \rangle. \]  

The first exponent in the integrand in (5) is the product of independent one-atomic factors. The second exponent does not decompose into a similar product. However, this exponent can be represented as a functional integral of the expression factorized by atomic coordinates:

\[ Z[\varphi(r)] = e^{\frac{BN}{N_\lambda^2N(0)}} \int (\nu) \left( \prod_{k=1}^{N_\lambda^2} \frac{d^3r_k}{v} \right) \exp(-\beta \int \varphi(r) \, n(r) \, dr) \times \exp(-\frac{\beta}{2} \int \nu(r - r') \, n(r) \, n(r') \, dr \, dr'). \]  

where

\[ F_1(x(k), y(k), \{\varphi(r)\}) = \int (\nu) \frac{dr}{v} e^{-\beta \varphi(r)} \times \exp\left(i \sum_{k \in \Omega/2} \sqrt{\frac{2\nu |k|}{v}} \left[ x(k) \cos(kr) + y(k) \sin(kr) \right]\right). \]  

\( x(k), y(k) \) are auxiliary variables that appeared as a result of the Stratonovich-Hubbard transformation, \( \Omega/2 \) is the half-space of the space of wave vectors \( \Omega \) obtained as a result of its dissection by an arbitrary plane passing through the origin \( k = 0 \).

The functional \( F_1(x(k), y(k), \{\varphi(r)\}) \) allows a obvious physical interpretation: it is equal to the configuration integral of one particle in a complex external field \( \Psi(r) \):

\[ \Psi(r) = \varphi(r) - i \sum_{k \in \Omega/2} \sqrt{\frac{2\nu |k|}{v}} \left[ x(k) \cos(kr) + y(k) \sin(kr) \right]. \]  

This external field consists of two parts: the “real” external field \( \varphi(r) \) and the artificial purely imaginary field due to the exclusion of interatomic interactions and presented as a Fourier series with coefficients \( \sqrt{\frac{2\nu |k|}{v}} x(k), \sqrt{\frac{2\nu |k|}{v}} y(k) \). The expression \( F_1(x(k), y(k), \{\varphi(r)\}) \) is the configuration integral of the classical ideal gas located in the complex external field \( \Psi(r) \).

2. The relationship between the external field and the spatial distribution of particles

We expand the external field \( \varphi(r) \) in a Fourier series

\[ \varphi(r) = \frac{1}{v} \sum_{k \in \Omega} \tilde{\varphi}(k) e^{ikr}, \]  

\[ \varphi(0) + \frac{2}{\nu} \sum_{k \in \Omega/2} \{	ilde{\varphi}_1(k) \cos(kr) - \tilde{\varphi}_2(k) \sin(kr)\}. \]  

\[ \begin{align*}
\tilde{\varphi}_1(k) &= 2 \nu |k| \int_{\Omega/2} \frac{dr}{v} e^{-\beta |k| r} \cos(kr) \\
\tilde{\varphi}_2(k) &= 2 \nu |k| \int_{\Omega/2} \frac{dr}{v} e^{-\beta |k| r} \sin(kr). 
\end{align*} \]  

Here
\[ \bar{\varphi}(\mathbf{k}) = \int_{(V)} \varphi(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} = \bar{\varphi}_1(\mathbf{k}) + i \bar{\varphi}_2(\mathbf{k}). \]  

Substitute this expression for \( \varphi(\mathbf{r}) \) into the formula (8) and get

\[ F_k(x, y, \{ \varphi(\mathbf{r}) \}) = \exp \left[ -\frac{\beta \bar{\varphi}^{(0)}}{v} \int_{(V)} \frac{d \mathbf{r}}{v} \exp \left[ \sum_{\mathbf{k} \in \Omega/2} \left[ z_1(\mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{r}) + z_2(\mathbf{k}) \sin(\mathbf{k} \cdot \mathbf{r}) \right] \right] \right], \]

where

\[ \begin{cases} 
    z_1(\mathbf{k}) = i \left( \sqrt{\frac{2 \beta \bar{\varphi}^{(0)}}{v}} x(\mathbf{k}) + i \frac{2 \beta}{v} \bar{\varphi}_1(\mathbf{k}) \right), \\
    z_2(\mathbf{k}) = i \left( \sqrt{\frac{2 \beta \bar{\varphi}^{(0)}}{v}} y(\mathbf{k}) - i \frac{2 \beta}{v} \bar{\varphi}_2(\mathbf{k}) \right). 
\end{cases} \]

This integral is a functional of the functions \( z_1(\mathbf{k}) \) and \( z_2(\mathbf{k}) \) and can be calculated using Weyl’s ergodic theorem \([3]\) by analogy with \([4]\). As a result, in the thermodynamic limit, we have

\[ \ln \left[ \bar{\varphi}_1^{(0)}(0) \right] = \frac{1}{1 + n \beta \bar{\varphi}(\mathbf{r})}. \]

Passing from summation to integration over wave vectors according to the rule

\[ \sum_{\mathbf{k} \in \Omega/2} \ldots = V \int_{k \in \Omega/2} \frac{d \mathbf{k}}{(2\pi)^3} \ldots = \frac{V}{2} \int_{k \in \Omega} \frac{d \mathbf{k}}{(2\pi)^3} \ldots, \]

we get the final expression for the logarithm of the generating functional of the system

\[ \ln Z(\varphi(\mathbf{r})) = N \ln \left( \frac{e}{n^3} \right) + \left( \frac{RN}{2} \right) \left[ v(0) - n \bar{v}(0) \right] - \beta n \bar{\varphi}(0) \]

\[ + \frac{n \beta^2}{N} \sum_{k \in \Omega/2} \left[ (\bar{\varphi}_1^2(k) + \bar{\varphi}_2^2(k)) \frac{1}{1 + n \beta \bar{\varphi}(\mathbf{k})} \right] \]

\[ - \sum_{k \in \Omega/2} \ln[1 + n \beta \bar{\varphi}(\mathbf{k})]. \]

The variational derivatives of \( \ln Z(\varphi(\mathbf{r})) \) with respect to the external field \( \varphi(\mathbf{r}) \) make it possible to find both the local density of the number of particles taking into account the removal of the degeneracy caused by the translational symmetry of its Hamiltonian and its correlation functions \([1]\).

### 3. The Local Distribution Density

The logarithm of the generating functional (16) consists of two terms

\[ \ln Z(\varphi(\mathbf{r})) = \ln Z_0 + \ln Z_1(\varphi(\mathbf{r})), \]

the first of which is the logarithm of the partition function in the absence of an external field \( \ln Z_0 \), and the second

\[ \ln Z_1(\varphi(\mathbf{r})) = -\beta n \bar{\varphi}(0) + \frac{n \beta^2}{2} \int_{k \in \Omega} \frac{d k}{(2\pi)^3} \frac{\bar{\varphi}_1^*(k) \bar{\varphi}(k)}{1 + n \beta \bar{\varphi}(\mathbf{k})}. \]

is due to the reaction of the system to an external field. Returning to the coordinate representation of the external field, we find

\[ \ln Z_1(\varphi(\mathbf{r})) = -n \beta \int \varphi(\mathbf{r'}) \, d \mathbf{r'} \varphi(\mathbf{r'}) + \frac{n \beta^2}{2} \int_{k \in \Omega} \frac{d k}{(2\pi)^3} \left[ \int \int d \mathbf{r'} d \mathbf{r''} \varphi(\mathbf{r'}) \varphi(\mathbf{r''}) e^{-\mathbf{k} \cdot \mathbf{r'}} e^{i \mathbf{k} \cdot \mathbf{r''}} \right] \frac{1}{1 + n \beta \bar{\varphi}(\mathbf{k})}. \]

We find the variational derivative of the generating functional with respect to the external field...
\[
\frac{\partial \ln Z_1(\varphi(r))}{\partial \varphi(r)} = -n\beta \int dr' \delta(r' - r) + \frac{n\beta^2}{2} \frac{d}{d\varphi(r)} \left[ e^{ik(r-r)} + e^{-i(k(r-r))} \right] \frac{1}{1 + n\beta \vartheta(k)}. \tag{20}
\]

Using (6), we find the relationship between the external field and the distribution of particles in space
\[
\langle \varphi(r) \rangle = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \int dr' \varphi(r') \left[ e^{ik(r-r')} + e^{-i(k(r-r'))} \right] \times \left[ 1 - \frac{n\beta \vartheta(k)}{1 + n\beta \vartheta(k)} \right]. \tag{21}
\]

So far as
\[
\int \frac{d^3k}{(2\pi)^3} e^{i(k(r-r')} = \delta(r - r'), \tag{22}
\]
then
\[
\langle n(r) \rangle = n - n\beta \varphi(r) + \frac{n\beta}{2} \int \frac{d^3k}{(2\pi)^3} \vartheta(k) \cos\left[ \frac{n\beta}{2} \right]. \tag{23}
\]

Note that the deviation of the local density \(\langle n(r) \rangle\) from the average density \(n\) has the form of a convolution integral
\[
\langle n(r) \rangle - n = n \int Q(n, \beta, r, r') \varphi(r') dr', \tag{24}
\]
where
\[
Q(n, \beta, r, r') = -\beta \delta(r - r') + \beta \int \frac{d^3k}{(2\pi)^3} [\varphi(r') \cos(k(r-r'))] \tag{25}
\]
is the kernel of the integral transformation, which depends not only on the coordinate difference \(r - r'\), but as well on the average density of the number of particles \(n\), inverse temperature \(\beta\) and the Fourier transform of the interatomic potential \(\vartheta(k)\).

4. The radial distribution function
Using (24), we find the second variational derivative of the generating functional with respect to the external field
\[
\begin{align*}
-\frac{1}{\beta} \frac{\partial^2 \ln Z_1(\varphi(r))}{\partial \varphi(r) \partial \varphi(r')} &= \frac{\delta(n(r))}{\delta \varphi(r)} = -n\beta \delta(r - r') \\
+ &n\beta \int_{k \in \Omega} \frac{d^3k}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \cos(k(r-r')) \vartheta(k) \tag{26}
\end{align*}
\]
The second variational derivative determines the correlations in the density distribution \([5]\]
\[
\begin{align*}
-\frac{1}{\beta} \frac{\partial^2 \ln Z_1(\varphi(r))}{\partial \varphi(r) \partial \varphi(r')} &= -\beta [\rho^{(2)}(r, r') - \langle n(r) \rangle \delta(r - r') - \langle n(r') \rangle \delta(r - r')] \\
\tag{27}
\end{align*}
\]
where
\[
\rho^{(2)}(r, r') = \langle n(r) \rangle \langle n(r') \rangle g^{(2)}(r, r') \tag{28}
\]
is the two-particle Born-Green-Yvon distribution function, \(g^{(2)}(r, r')\) is the pair correlation function, which in the case of a homogeneous isotropic medium is called the radial distribution function \(g(|r - r'|)\).

In the latter case \(\langle n(r) \rangle = n\). Taking into account (26), (27) and (28) we obtain the expression for the radial distribution function
\[
\rho^{(2)}(r, r') = \langle n(r) \rangle \langle n(r') \rangle g(|r - r'|). \tag{29}
\]

After integration over angular variables, the resulting expression will take the form
\[
\rho^{(2)}(r, r') = 1 - \int_{k \in \Omega} \frac{d^3k}{(2\pi)^3} \cos(kR). \tag{29}
\]
where $\mathbf{k} = |\mathbf{k}|$, $R = |\mathbf{R}|$. The function $n\beta\tilde{v}(k)/(1 + n\beta\tilde{v}(k))$ has two types of singular points on the complex plane $k$.

1. Singular points of the Fourier transform $\tilde{v}(k)$ of the interatomic potential $v(r)$; this function is non-negative on the real axis (Dobrushin-Ruelle-Fisher criterion [6, 7, 8]) and even. Suppose that all the singular points of the function $\tilde{v}(k)$ are poles. Then these points are removable features that do not contribute to the integral in the expression.

2. Roots of the equation

$$1 + n\beta\tilde{v}(k) = 0. \quad (31)$$

These roots substantially depend not only on the type of interatomic potential, but also on the average density $\rho$ and temperature $T = 1/\beta$.

### 5. Radial distribution function for the double Yukawa model potential

Consider, as an example of a thermodynamic system, a fluid whose particles interact through the double Yukawa potential

$$v(r) = \frac{1}{4\pi r} [A\exp(-ar) - B\exp(-br)]. \quad (32)$$

Fourier transform of this potential has the following form

$$\tilde{v}(k) = \frac{A}{a^2 + k^2} - \frac{B}{b^2 + k^2}. \quad (33)$$

Here we should take into account the Dobrushin-Ruelle-Fisher criterion [6, 7, 8]. For the existence of a thermodynamic limit, it is necessary and sufficient that interatomic interactions belong to the class of stable interactions. In the case of the existence of the Fourier transform of the interatomic potential, this criterion has the form [9]

$$\tilde{v}(k) \geq 0. \quad (34)$$

This imposes the following [10] restrictions on potential parameters (32):

$$A > B, \quad a > b, \quad Ab^2 - Ba^2 > 0. \quad (35)$$

We now introduce the variables depending on the parameters of the potential, the average density, and temperature

$$A - B = C, \quad Ab^2 - Ba^2 = D, \quad a^2 + b^2 + n\beta A - n\beta B = c, \quad a^2b^2 + n\beta Ab^2 - n\beta Ba^2 = d. \quad (36)$$

Calculating the integral in the expression (30), we obtain the expression for the radial distribution function

$$g(R) = 1 - \frac{\beta}{2\pi R} [C_1\exp(-\lambda_1 R) + C_2\exp(-\lambda_2 R)], \quad (37)$$

where

$$C_1 = \frac{c\lambda_1 - D}{2(\lambda_1^2 - \lambda_1^2)}, \quad C_2 = \frac{c\lambda_2 - D}{2(\lambda_2^2 - \lambda_2^2)}, \quad \lambda_1 = \frac{\sqrt{c - c\sqrt{c^2 - 4d}}}{\sqrt{2}}, \quad \lambda_2 = \frac{\sqrt{c + c\sqrt{c^2 - 4d}}}{\sqrt{2}}. \quad (38)$$

Note that for any values of the potential parameters (32), density and temperature, the Dobrushin-Ruelle-Fischer condition excludes the oscillating behavior of the radial distribution function. It should be noted that this conclusion contradicts the results obtained in the work [11]. The oscillations of the radial distribution function found in [11] are due to the use of the parameters of interatomic potentials beyond their
applicability. The same remark applies to attempts to describe a second-order phase transition in the case 
\[ \min |g| < 0 \] [12].

6. Conclusion
The expression (16) for the generating functional, which is valid for an arbitrary static external field \( \varphi(\mathbf{r}) \), can be used for calculating of the correlation functions of many-particle systems. However, if the time scale at which the external dynamic field \( \varphi(\mathbf{r}, t) \) noticeably changes is much longer than the time between particle collisions, then it is suitable for calculating of the response functions of the system to external fields.

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