The Asymptotic Expression for the Structure Function of Interacting Particles

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It is desirable that we calculate the structure function of interacting particles without using any approximation except the fact that the number of particles is extremely large.

Denoting by \( Q_N(E_p) \) the volume of the set of points the potential energy corresponding to which is less than \( E_p \) in the configurational space of \( N \) particles, the problem to find the asymptotic expression of \( Q_N(E_p) \) as \( N \to \infty \) can be partly solved as follows.

We assume that

\[
E_p = \sum_{i=N}^{i=N-1} \sum_{j=1}^u(r_{ij})
\]

where \( u(r_{ij}) \) is the potential energy of the pair of particles \( i \) and \( j \) as a function of their distance apart \( r_{ij} \),

\[
u(r_{ij}) = 0 \quad \text{for} \quad r_{ij} \geq r_1
\]

and for

\[
u(r_{ij}) < r_1
\]

either Case (I)

or Case (II)

\[
u(r_{ij}) < A \quad \text{for} \quad 0 < r_0 < r_{ij}
\]

\[
u(r_{ij}) = \infty \quad \text{for} \quad r_{ij} < r_0
\]

where \( r_1, r_0, \) and \( A \) are constants.

Writing

\[
Q_N(E_p) = g(v)F_N(E_p)
\]

where \( v \) is the volume of the container and \( g(v) \) is the volume of the configurational space accessible by the system (in the case (I) \( v = \frac{\nu^N}{N!} \), \( F_N(E_p) \) may be interpreted as the distribution function of \( E_p \), and our problem reduces to that of the theory of probability.

Introducing the new variable \( \chi_N = E_p^{1/\nu} \) and suitably changing the origin of the energy, we find that the every moment of \( \chi_N \) whose distribution function is \( G_N(\chi_N) = E_p^{1/\nu} \) tends to that of the Gaussian distribution as \( N \to \infty \) fixing the density \( \rho = N/v \).

It can be proved that the Taylor expansion of the characteristic function of \( G_N(\chi_N) \) converges uniformly with respect to \( N \) for fixed \( \rho \). Accordingly, the characteristic function of \( G_N(\chi_N) \) tends to that of Gauss, which results in

\[
F_N(E_p) \sim 1 / \sqrt{2\pi N\mu_2} \times \int_{-\infty}^{E_p} \exp\left(-\frac{z^2}{2N\mu_2}\right) dz
\]

where

\[
\mu_2 = 2\rho \int_0^\infty u^2(r) r^2 dr.
\]

This is rigorous so long as \( E_p \) is arbitrarily fixed as \( N \to \infty \). But if we want to make use of this to the statistical mechanics (for example, the expression for entropy), \( E_p \) must be increased proportionally to \( N \). This fact seems to make the direct application of this result to the statistical mechanics in the lower temperature range very doubtful. Under the assumption (I) however, it is found that our method gives the correct value to the free energy in the limit \( V^\rho /kT \to 0 \), which may be compared with the well-known Mayer's theory of imperfect gas where the contribution from higher irreducible integrals becomes zero in the limit \( \rho/kT \to 0 \).
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