ASYMPTOTIC METHODS AND JOINING OF ASYMTOTICS IN THE KINETIC THEORY OF CONDENSED MATTER

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The article is devoted to application of asymptotic methods in the theory of time–dependent pair distribution functions

The kinetic theory remains still the urgent problem of the statistical mechanics. In particular, the two–particle kinetic distribution functions, which described the kinetic of relative motion of two particles, is very important. However, the evaluation of these functions is very difficult task, which decides by some approximation methods.

At first, we will use the asymptotic estimation the binary time correlation function suitable for description of the high–frequency domain (domain of short times).

This binary distribution function represents the unconditional probability density of mutual position of two particles at the initial moment of time radius–vector $\mathbf{r}_0$ and at the moment t with $\mathbf{r}$.

It is defined as a mean value of the form [1,2]

$$F(\mathbf{r}_0,\mathbf{r},t) = N^{-1}\sum_{i\neq j}\left\langle \delta(\mathbf{r}_0 - \mathbf{r}_{ij}(0))\delta(\mathbf{r}-\mathbf{r}_{ij}(t))\right\rangle \tag{1}$$

and has the following properties

$$F(\mathbf{r}_0,\mathbf{r},0) = ng(r_0)\delta(\mathbf{r}-r_0), \tag{2}$$

$$F(\mathbf{r}_0,\mathbf{r},t\to\infty) = N^{-1}ng(r_0)ng(r), \qquad n=\frac{N}{V}. \tag{3}$$

Here $\delta(\mathbf{r})$ is the Dirac′s δ–function, V is volume of system, $g(r)$ is binary distribution function.

By taking the average of (1) over canonical distribution the asymptotic exactly at $t\to 0$ expression can be obtained

$$F(\mathbf{r}_0,\mathbf{r},t) = (g(\mathbf{r}_0)g(\mathbf{r}))^{1/2}\, n\langle a\rangle_0, \quad a=\delta(\mathbf{r}_0-\mathbf{r}-vt), \tag{4}$$

here v is the particle velocity.

Symbol $\langle\ldots\rangle_0$ denotes the averaging over equilibrium velocity distribution function the resulting expression is [3].

$$F(\mathbf{r}_0,\mathbf{r},t) = g(r)n\left(\frac{\beta\mu}{2\pi t^2}\right)^{3/2}\exp\left(\frac{-\beta\mu(\mathbf{r}-\mathbf{r}_0)^2}{2t^2}\right), \ \beta=(k_BT)^{-1}, \tag{5}$$

here μ is reduced mass of two particles.

In another form we write

$$F(\mathbf{r}_0,\mathbf{r},t) = ng(r)f(\mathbf{r}_0,\mathbf{r},t). \tag{6}$$

The Fourier transform of function $f(\mathbf{r}_0,\mathbf{r},t)$ are

$$f(\mathbf{k},t)=\exp(-k^2t^2/2\mu\beta)\,, \tag{7}$$

$$f(k,\omega)=\left(\beta\mu/2\pi k^2\right)^{1/2}\exp(-\beta\mu\omega^2/2k^2)\,. \tag{8}$$

These formulas describes case of free–particles systems. The functions $f(\mathbf{r}_0,\mathbf{r},t),\ f(k,t)$ and $f(k,\omega)$ are all Gaussian functions in the appropriate variables.

The function $f(\mathbf{k},\omega)$ is dynamics structure factor for the relation motion two particles.

Now we consider the opposite case of long times or low frequencies.

In this domain the binary distribution function is governed by diffusion equation

$$\frac{\partial f(\mathbf{r}_0,\mathbf{r},t)}{\partial t}=-D\Delta_r^2 f(\mathbf{r}_0,\mathbf{r},t)\,. \tag{9}$$

Where D is the coefficient of mutual diffusion the two particles. This equation is to be solved with initial condition

$$f(\mathbf{r}_0,\mathbf{r},0)=\delta(\mathbf{r}-\mathbf{r}_0)\,. \tag{10}$$

One finds

$$f(\mathbf{r}_0,\mathbf{r},t)=(4\pi Dt)^{-3/2}\exp(-(\mathbf{r}-\mathbf{r}_0)^2/4Dt)\,, \tag{11}$$

$$f(k,t)=\exp(-Dk^2t)\,, \tag{12}$$

$$f(k,\omega)=\frac{1}{\pi}\frac{Dk^2}{\omega^2+(Dk^2)^2}\,. \tag{13}$$

It is not difficult to obtain the next interpolated formula $(0\le t\le\infty)$

$$f(k,t)=f(-k^2a(t))\,,$$

where

$$a(t)=\frac{t^2}{2\beta\mu+tD^{-1}} \tag{14}$$

It should be noted that for $t\to 0$

$$f=\exp\left(-\frac{k^2t^2}{2\beta\mu}\right) \tag{15}$$

and for $t\to\infty$

$$f=\exp(-k^2Dt)\,. \tag{16}$$

The function $\exp(-ak^2)$ in coordinate representation has the form

$$\int \exp(-ak^2)e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}_0)}d\mathbf{k}=\frac{1}{(4\pi a)^{3/2}}\exp\left(-\frac{(\mathbf{r}-\mathbf{r}_0)^2}{4a}\right) \tag{17}$$

Now we consider the joining of asymptotics (8) and (13), that is

$$f_1(k,\omega)=\left(\frac{\beta\mu}{2\pi k^2}\right)^{1/2}\exp\left(-\frac{\beta\omega^2}{2k^2}\right) \tag{18}$$

and

$$f_2(\mathbf{k},\omega)=\frac{1}{\pi}\frac{Dk^2}{\omega^2+(Dk^2)^2}\,. \tag{19}$$

The procedure is similar to the same which is used by M. Planck at derivation his famous formula for intensity of radiation of black body via joining of asymptotics due to Rayleigh–Jeans and Vin (see for example [4]). Taking into account relation $f(\mathbf{k},\omega)=f_1(1+f_2/f_1)^{-1}$ in result we find

$$f(\mathbf{k},\omega)=\frac{(\beta\mu/2\pi k^2)^{1/2}\exp(-\beta\mu\omega^2/2k^2)Dk^2}{Dk^2+(\beta\mu/2\pi k^2)^{1/2}\exp(-\beta\mu\omega^2/2k^2)\pi(\omega^2+(Dk^2)^2)}\,. \tag{20}$$

At $\omega\to\infty$ we obtain (18) and at $\omega\to 0$ we find (19).

In theory of viscosity for polymer solution may be used asymptotic methods and Pade–approximation approach (see, for example [4], [5]).

Let in dilute solution the density dependence of viscosity represents asymptotically by the virial expansion

$$\mu=\eta/\eta_s=1+a_1c+a_2c^2\,, \tag{21}$$

where η_s, is viscosity of the solvent, c is the concentration of the solute, η is the solution viscosity.

Pade–approximation is defined as

$$\mu=\frac{1+\beta c}{1-\gamma c}\,. \tag{22}$$

The coefficients β and γ is expressed via the coefficients a_1 and a_2 of the virial expansion (21),

$$\beta=\frac{a_1^2-a_2}{a_1},\ \ \gamma=\frac{a_2}{a_1} \tag{23}$$

As example we consider the suspension of hard spherical particles. In this case $\mu=1+2{,}5c+5c^2$ and $\beta=0{,}5,\ \gamma=2$ and there fore

$$\mu=\frac{1+0{,}5c}{1-2c}\,. \tag{24}$$

This formula describes the concentration dependence at the high concentration very well.

In 1916 A. Einstein obtain μ as $\mu=1+5/2c$. There fore $a_1=2{,}5$ and $\mu=\dfrac{1}{1-2{,}5c}$.

In above mentioned wore A. Einstein at first applied the hydrodynamics to molecular objects. At present this Einstein result dive rise to the generalized molecular hydrodynamics [6].

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