SIMPLE MODEL FOR THE CALCULATION OF THE COEFFICIENT OF SELF-DIFFUSION IN A LIQUID

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The coefficient of self-diffusion in three-dimensional classical liquid is computed approximately from the hierarchy of kinetic equations for the time-correlation functions (TCF).

The coefficient of self-diffusion D_s of a molecule can be obtained from the TCF $\pi(t) = \langle p_1(0)p_1(t)\rangle/\langle p_1^2\rangle$ of momentum $p_1(t)$ at time t of a chosen particle in a fluid by $D_s = (kT/m)\lim_{z\to+0}\tilde{\pi}(z)$, where $\tilde{\pi}(z) = \int_0^\infty \mathrm{d}t\cdot\exp(-zt)\pi(t)$, where m is the mass of a particle and kT the thermal energy. Here we shall obtain the formula for D_s from the small-z behavior of the hierarchy of the equations for TCF.

Zwanzig was the first to succeed in deriving a kinetic equation from the Liouville equation [1]: $\pi'(t) = -\int_0^t \mathrm{d}\tau K(\tau)\pi(t-\tau)$, where the memory function is

$$K(\tau) = \langle p_1\hat{\mathcal{L}}\exp\{\mathrm{i}\mathcal{L}_{22}^{(1)}\tau\}\hat{\mathcal{L}}p_1\rangle/\langle p_1^2\rangle\,, \qquad \mathcal{L}_{22}^{(1)} = P\hat{\mathcal{L}}P, \qquad \hat{\mathcal{L}} = -\mathrm{i}\hat{L}\,, \qquad \hat{\mathcal{L}} = \sum_{j=1}^{N}\frac{1}{m}p_j\nabla_j - \sum_{i\neq j=1}^{N}\nabla_j u(j,i)\nabla_{p_j}\,,$$

$$P = 1 - \Pi\,, \qquad \Pi = \frac{p_1\rangle\langle p_1}{\langle p_1^2\rangle}\,,$$

Π is the projection operator, $\hat{L}$ is the ordinary Liouville operator and $u(i,j)$ is the interparticle potential. If we use the identity [2]

$$\exp\{t(A+B)\} = \exp(tA) + \int_0^t \mathrm{d}u\,\exp\{(t-u)A\}\,B\,\exp\{u(A+B)\}\,,$$

for the arbitrary operators A and B, we can obtain an expansion of $K(t)$:

$$K(t) = \omega^2 f(t) + \sum_{n=1}^{\infty}(-1)^{n+1}\int_0^t \mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\ldots\int_0^{t_{n-1}}\mathrm{d}t_n\,\pi'(t-t_1)\pi'(t_1-t_2)\ldots\pi'(t_{n-1}-t_n)\pi''(t_n)\,,$$

where $\omega^2 = \langle F_1^2\rangle/\langle p_1^2\rangle$, $f(t) = \langle F_1\exp(\mathrm{i}\hat{\mathcal{L}}t)F_1\rangle/\langle F_1^2\rangle$, $F_1 = -\sum_{j>1}^{N}\nabla_1 u(1,j)$ is the total force on a chosen particle.

Now one can write the Laplace transform of $K(t)$ in the form

$$\tilde{K}(z) = \omega^2\tilde{f}(z) + z\sum_{n=1}^{\infty}\{1 - z\tilde{\pi}(z)\}^{n+1}\,. \tag{1}$$

Then for $z\to+0$ we obtain $\tilde{K}(z) \approx \omega^2\tilde{f}(z)$ and $\tilde{\pi}(z) \approx \{z+\omega^2\tilde{f}(z)\}^{-1}$. Following Zwanzig [1] we may write the kinetic equation for the TCF $f(t)$: $f'(t) = -\int_0^t \mathrm{d}\tau\cdot V(\tau)f(t-\tau)$, where

$$V(\tau) = \langle F_1\hat{\mathcal{L}}\exp\{\mathrm{i}\mathcal{L}_{22}^{(2)}\tau\}\hat{\mathcal{L}}F_1\rangle/\langle F_1^2\rangle, \quad \mathcal{L}_{22}^{(2)} = Q\hat{\mathcal{L}}Q, \quad Q = 1 - R, \quad R = \frac{F_1\rangle\langle F_1}{\langle F_1^2\rangle}\,,$$