CALCULATION OF THE VELOCITY AUTO-CORRELATION FUNCTION BY MOLECULAR DYNAMICS IN LIQUID COPPER

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Abstract.

To be able to derive all macroscopic properties of the condensed system, it is necessary to know the pair wise particles potential of the system. In order to study these properties, a molecular dynamic experiment has been perforemd on liquid copper, at 1393 K. For the above mentioned experiment the pair potential has been calculated by inverting the Week-Chandler-Anderson (WSA) perturbation theory. With this potential the velocity auto-correlation function f(t), the pair correlation function g(r) and the transport quantities like self-diffusion coefficient D were calculated. The calculated data were copmared to the experimental one and the agreement was rather good.

I. Introduction

The behaviour of particles in the condensed system can be described by the classical Newton's equation of motion. To perform computers simulation experiment in molecular dynamics the principal demand is to integrate the equation of motion.

$$m \frac{d^2 r_i}{dt^2} = - \sum_{j \neq i} \nabla \varphi(r_{ij}); \quad (r = r_{ij} = |\underline{r}_i - \underline{r}_j|) \qquad (1)$$

For the molecular dynamics experiment it is necessary to know the pair potential $\varphi(r)$. Exept for analytical expression of $\varphi(r)$ one also can use the numerical values of pair potential. In liquid monatomic structure, as liquid copper, the slowly varying attractive pair potential $\varphi_{att}(r)$ can be treated as a perturbation on the reference hard sphere potential $\varphi_{\sigma}(r)$, so that $^{1)}$,

$$\varphi(r) = \varphi_{\sigma}(r) + \varphi_{att}(r) \qquad (2)$$

In order to get $\varphi(r)$ we started with the experimental structure factor S (q) on liquid copper, at temperature 1393 K$^{2)}$. To avoid the uncertainty for the small q-data in S(q), instead of the random-phase approximation (RPA) $^{3)}$ we applied the general RPA taking into account the correlation effects between electrons $^{4)}$. The derived pair potential, by above procedure, has expected shape for monatomic liquids $^{5)}$.

II. The method of molecular dynamics

The basic assumption in molecular dynamics experiment is that the particles interact between themselves through the pair wise forces. In our computer simulation, the experiment on liquid copper, with mass m ($m = 1.08 \times 10^{-25}$ kg) we considered a system of 256 particles in a cubic box with periodic boundary conditions. From the number of density, for copper at temperature T = 1393 K ($\rho = 7.487 \times 10\ m^{-3}$) and chosen number of particles N, the length L of cubic box was defined (L = 11.3 Å). The computer simulation with a few hundred particles gives a submicroscopic level of the structure, which is rather limited approximation in the case of the ordinary thermodynamics consideration. It means, if we want to decrease the error in calculations of different quantities, it is necessary to increase a number of particles in considered system.

As it is mentioned above the forces between particles are pair wise additive and the total forces on the particle at origin is a sum of forces from the surrounding particles within the sphare of radius r_c, $|\underline{r}_i - \underline{r}_j| \leqslant \underline{r}_c$, ($r_c \leqslant \frac{L}{2}$). With selected radius r_c we defined a number of neighborous particles which interact between themselves and gain a reasonable computer time.

Since the pair potential was defined numberically 5) we were able to calculate the positions r_i and velocities v_e, eq. 1. The initial configurations $r_1, \ldots, r_N$ were chosen as a lattice points of the FCC structure with corresponding L. Since we know the $r_1, \ldots, r_N$, it was possible for us to evaluate the accelerations a. These calculations could be performed using a random number generator. To calculate new positions and velocities we used the algorithm introduced by Beeman 6) which was extended by Ebbsjö 7) in the following form,

$$r(t + \Delta t) = \underline{r}(t) + \underline{v}(t)\,\Delta t + \left[4\underline{a}(t) - \underline{a}(t - \Delta t)\right] * \frac{(\Delta t)^2}{6}$$

$$\underline{v}(t + \Delta t) = v(t) + \left[2a(t + \Delta t) + 5\underline{a}(t) - \underline{a}(t - \Delta t)\right] * \frac{(\Delta t)}{6} \qquad (3)$$

The magnitude of the time step Δt is of the order of 10^{-14} sec. For the liquid copper the time step Δt was chosen according to the criterion $\omega_E \Delta t = 0.3$ 8). To integrate the equation of motion of the system, which starts from the initial equilibrium configurations, the number of the integration steps is of the order 10^2 to 10^3. With this values we obtained the oscillation time of particles, 10^{-12} sec, that means that we are able to study the dynamics of liquids. For new configurations of the particles the accelerations again were calculated using expressions

$$\underline{r}_i(t) = r_i(t - \Delta t) + 0.5\,\underline{a}_i(t - \Delta t) * (\Delta t)^2 \text{ and } \underline{v}_i(t) = \underline{a}_i(t) * \Delta t \qquad (4)$$

With these vectors, each of a size of 3N, we used the algorithm, eq. 3, for the determination of new positions and velocities. With 160 integration steps we obtain the positions $r_i, \ldots, r_{256}$, as well as the velocities $v_i, \ldots, v_{256}$ what has been recorded.

Since the pair potentials $\varphi(r_{ij})$ are aditive it is possible to define the potential energy of N atoms as

$$\varphi(r^N) = \sum_{i<j} \varphi(r_{ij}) \tag{5}$$

In the sum r_{ij} is interpreted as a distance between r_i or r_j and the nearest image particle j whichever is closer.

With this assumption the molecular dynamics "experiments" are more complete generally more precise than the corresponding real experiments$^{9)}$ and give all basic quantities of the liquid state. Introducing a Hamiltonian of the system we can calculate: the canonical partition function Z_N

$$Z_N = \frac{1}{N!\,\lambda^{3N}} \int e^{-\beta\varphi(r^N)}\, d\underline{r}_1, \ldots, d\underline{r}_N \;;$$

$$\lambda = \frac{h}{\sqrt{2\pi m \beta^{-1}}} \;; \quad \beta = \frac{1}{K_B T} \tag{6}$$

and the pair correlation function g(r),

$$g(r) = \frac{1}{\rho^2 (N-2)!\,\lambda^{3N} Z_N} \int e^{-\beta\varphi(r^N)}\, d\underline{r}_3, \ldots, d\underline{r}_N \tag{7}$$

One can also calculate the pair correlation function g(r) from the Fourier transform of S(q) and compare it with calculated, (eq. 7) in the region $0 < r < \frac{1}{2}L$ what is at the same time a good test of molecular dynamics experiment.

The real test of the computer simulation techniques is calculation of the time-dependent correlation function, i. e. the velocity auto-correlation function f(t) $^{10)}$ defined as

$$f(t) = \langle \underline{v}(t)\, \underline{v}(0) \rangle = \frac{1}{N} \sum_{i=1}^{N} \underline{v}_i(t)\, \underline{v}_i(0) = 0.5 \frac{d^2}{dt^2} \langle r_i^2 \rangle \tag{8}$$

where $\langle r_i^2 \rangle$ i. e. $\langle | \underline{r}_i(0) - \underline{r}_i(t) | \rangle^2$, is the mean square displacement of particle.

According to matrix data of $\underline{r}_i$ and $\underline{v}_i$ vectors, we can calculate the velocity auto-correlation function, for copper at 1393 K, and the results are shown in figure 1.

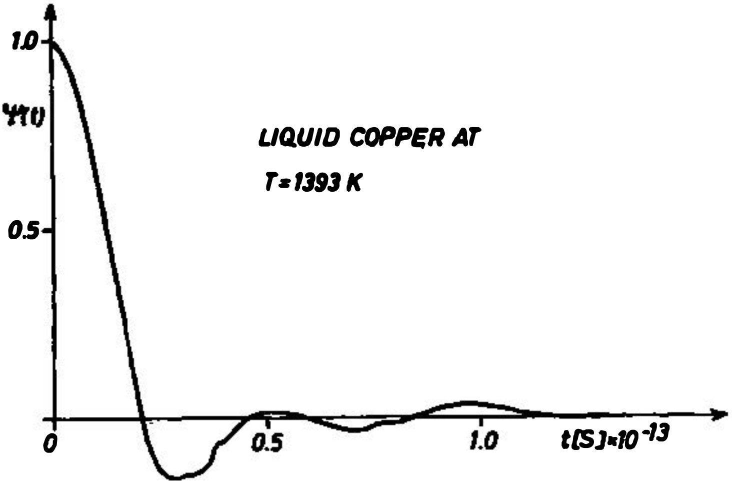

Figure 1.

The ratio $\Psi(t) = \frac{\langle \underline{v}(0)\ \underline{v}(t)\rangle}{\langle v(0)^2\rangle}$ which insure that the curve in figure 1 start with magnitude 1, ~~is given~~ on the ordinate.

The profile of the velocity auto-correlation function is expected, except for a large time where is rather overdamped.

The deviation at longer times is related to accumulated errors in numerical integration.

The transport coefficient D can be calculated as an integral of time-dependent function (Green-Kubo formula) 11).

$$D = \frac{1}{3}\int_0^\infty f(t)\,dt \qquad (10)$$

The diffusion coefficient can also be defined by the well known Einstein relation 12)

$$D = \frac{1}{\beta\zeta}$$

where ζ is the friction coefficient which according to the exact statistical mechanics treatment of transport properties depends on an integral which contains the products of a correlation function g(r), and the first and second derivatives of pair potential 12,5). In table 1 the self-diffusion coefficient D(cm²/sec) x 10^{-5} obtained according to eq. 9 and 10⁵⁾ are compared.

Table 1.

Liquid Cu	D(eq. 9)	D(eq. 10)	D(exp)
at 1393 K	1,7	6,53	4,22

The agreement is rather good for this macroscopic quantity.

Acknowledgement

We wish to thank to Professor P. Schofield and to colleagues Drs. Ingvar Ebbsjö and Thomas Kinell for their helpful discussions and computer programme.

References

1. H. C. Anderson, D. Chandler and J. D. Weeks, J. Chem. Phys., 56. 3812 (1972).
2. B. Kunsch (1979), private communications.
3. R. Brout, Phase Transitions, Amsterdam (1965).
4. T. Gaskell, Phys. Lett. 65A, 421 (1978).
5. Dj. Jović, M. Davidović and K. Chaturvedi, J. de Physique, 41, Colloque C-8, Supp. 8, 276 (1980).
6. D. Beemen, J. Comp. Phys., 20, 130 (1976).
7. I. Ebbsjö, Ph. Thesis, Umeå Universitet (1977).
8. P. Schofield, Comp. Phys. Com., 5, 17 (1973).
9. D. Levesque and L. Verlet, Phys. Rev. A2, 6.2514 (1970).
10. A. Rahman, Eds. by P. C. Gehlen, J. R. Beeler, R. I. Jaffee, Interatomic potentials and Simulation of Lattice Defects, P. Press, London (1972).
11. O. J. Eder, J. Chem. Phys. 66, 9.3866 (1977).
12. S. A. Rice and J. G. Kirkwood, J. Chem. Phys., 31. 901 (1959).