

5. Molecular dynamics based on the first order correction in the Wigner-Kirkwood expansion

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In 1932 Wigner ^(1, 2) derived quantum mechanical versions of the Liouville equation and of the canonical distribution in phase space. Both can be written as power series in \hbar^2 which reduce to the classical expression when $\hbar = 0$. The first few terms in the distribution function

$$f_w = f_o(1 + \hbar^2 A_1 + \hbar^4 A_2 + \dots); f_c = Q^{-1} \exp -\beta H_c \quad (1)$$

have served as a basis for the calculation of quantum corrections in almost classical systems ⁽³⁻⁵⁾.

Putting the correction terms in (1) into the exponent, one obtains - to first order in \hbar^2 - the quantum corrected Hamiltonian

$$H_Q = H_c - \hbar^2 A_1 / \beta \equiv H_c + \Delta H_Q \quad (2)$$

where $H_c = \sum_j p_j^2 / 2m + U(r_1, \dots, r_N)$; $\beta = (kT)^{-1}$,

U = Potential Energy

$$\Delta H_Q = \frac{\hbar^2}{24} \left\{ -\frac{\beta^2}{m^2} \left(\sum_j p_j \cdot \frac{\partial}{\partial r_j} \right)^2 U + \frac{3\beta}{m} \sum_j \frac{\partial}{\partial r_j} \cdot \frac{\partial}{\partial r_j} U - \frac{\beta^2}{m} \sum_j \frac{\partial}{\partial r_j} U \cdot \frac{\partial}{\partial r_j} U \right\}$$

Refs.(1,6,7) (3)

Corrections to the equilibrium properties can be obtained by first integration of (3) over the momenta and use of the effective potential so calculated in thermodynamic perturbation theory ⁽²⁾. The effective potential can in principle also be used in MC simulations. Alternatively the first (and second) correction terms can be evaluated in classical MD simulations ⁽⁵⁾.

In order to compute dynamical as well as equilibrium properties, it is necessary to use $H_c + \Delta H_Q$ as an effective Hamiltonian in the simulation with classical equations of motion. This can be justified by the following argument.

Since the system is in equilibrium we require that

$$\frac{dH_Q}{dt} = \sum_j \left(\dot{\mathbf{r}}_j \cdot \frac{\partial H_Q}{\partial \mathbf{r}_j} + \dot{\mathbf{p}}_j \cdot \frac{\partial H_Q}{\partial \mathbf{p}_j} \right) = 0 \quad (4)$$

(4) is satisfied if Hamilton's (classical) equations are valid:

$$\dot{\mathbf{r}}_j = \frac{\partial H_Q}{\partial \mathbf{p}_j}, \quad \dot{\mathbf{p}}_j = -\frac{\partial H_Q}{\partial \mathbf{r}_j} \quad (5)$$

$\ddot{\mathbf{r}}_j$ which is needed if one wishes to use the familiar Verlet or Leapfrog algorithms, is obtained from

$$\frac{d}{dt} \dot{\mathbf{r}}_i = \left(\sum_j \dot{\mathbf{r}}_j \cdot \frac{\partial}{\partial \mathbf{r}_j} + \dot{\mathbf{p}}_j \cdot \frac{\partial}{\partial \mathbf{p}_j} \right) \frac{\partial H_Q}{\partial \mathbf{p}_i} \quad (6)$$

Apart from the algebraic complexity, the simulation based on H_Q has some near-pathological properties resulting from the derivatives of the repulsive term in the Lennard-Jones 12-6 potential; particularly the derivative of the last term in (3) leads to a very rapid variation with distance in the repulsive range. To prevent occasional 'blow-ups' it proved necessary to incorporate a safety device whereby exceptionally large forces - say 20 x larger than the mean - are reduced in magnitude. With a safety device coming into operation for < 1% of the pair forces and a time step of 0.4×10^{-14} s the simulation was still quite stable for neon near the triple point (LJ-12-6).

The principal results reported were:

1. For the systems with a thermal de Broglie wavelength $\hbar / (mkT)^{1/2} > 2 \times 10^{-10}$ e.g. Ar, N₂, Ne (not too close to the triple point) the energy correction calculated in a completely classical MD simulation agrees with that obtained in a simulation based on (3)-(6). This is not true for the pressures.
2. Even when λ (de Broglie) $\sim 0.5 \times 10^{-10}$, e.g. for Ar near the triple point, the quantum corrections are not negligible.

3. The quantum corrections tends to reduce the diffusion constant.

References

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