When Quantum Effects Are Important – Feynman's Path Integral Method

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Feynman's Path Integral Method is a method to obtain quantum results from molecular simulations with classical equations. Real atoms and molecules are quantum objects with an uncertainty in their position. In ordinary classical simulations this effect is neglected, but in Feynman's method it is included.

As an example we have calculated the heat capacity of liquid helium at 4.2 K. At this temperature the quantum effects are large. In Fig. 1, the liquid heat capacity at saturated vapour pressure is shown. The red star displays that the heat capacity from Feynman's Path Integral Method gives the same value as the experimental one. The erroneous result from a classical simulation (black star) is much higher.

Heat capacity at 4.2 K

Experimental	17.9 J/molK
Feynman	17.9 J/molK
Classical	60.7 J/molK

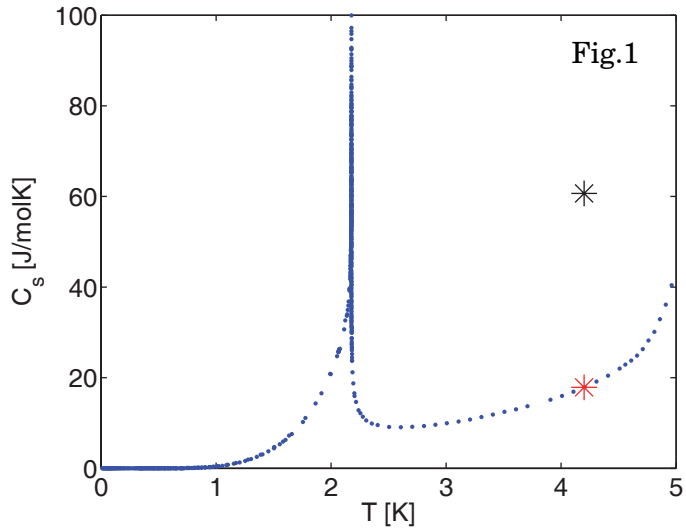

Fig.1

In Feynman's method, the classical exact positon of an atom is replaced by a "polymer" of "beads" connected by springs. The more extended the polymer, the more "smeared out" is the location of the atom.

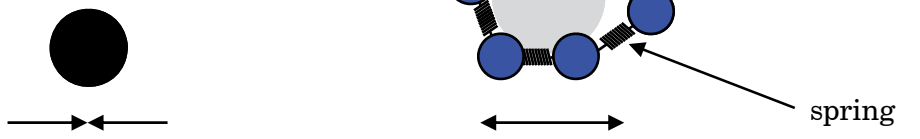

Fig.2

position x
classical atom

position $x + \Delta x$
quantum atom

In Fig. 3, two atoms are shown, each represented by a polymer of six beads. The lines denote real potential interactions between pairs of beads. Neighbour beads are bound together by harmonic springs whose force constants increase for increasing temperature, thereby contracting them to the same point in the high temperature limit, i.e. the classical case.

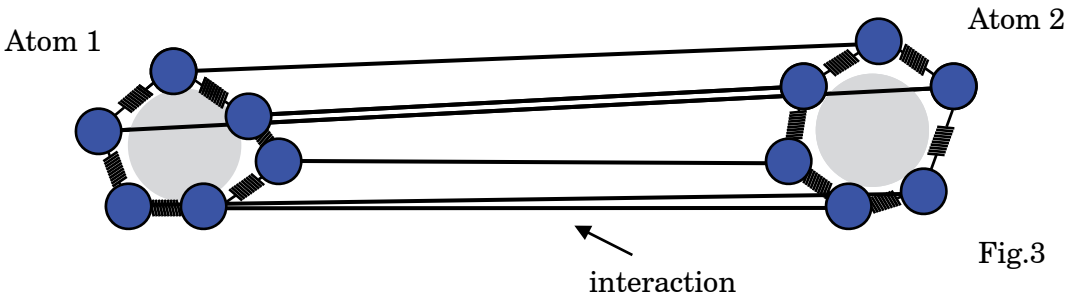

Fig.3

Say that we want to simulate a system comprised of N atoms. In classical physics the interaction between the atoms is described by a potential

$$V_{cl}\left(r_1, r_2, \ldots, r_N\right),$$

where r_i is the position of atom i. Using this potential in a Monte Carlo or Molecular Dynamics simulation, for instance the energy at a specific temperature may be obtained.

With Feynman's method each atom is replaced by a ring of P beads. The same function V_{cl} is used. The total potential energy is however now the average potential energy when all the beads are included. The first term is obtained by replacing the position of each atom by the position of bead number one of each atom, etc. Thus,

$$V = \frac{1}{P}\sum_{j=1}^{N} V_{cl}\left(r_{1,j}, r_{2,j}, \ldots, r_{N,j}\right)$$

where $r_{i,j}$ is the position of bead j of atom i.

Finally, the quantum mechanical spring energy is added to the total potential energy.

$$V = \frac{M}{2\beta^2\hbar^2} P\sum_{i=1}^{N} V_{\text{polymer ring for atom } i} \qquad V_{\text{polymer ring for atom } i} = \sum_{j=1}^{P} \underbrace{\left|r_{i,j} - r_{i,j+1}\right|^2}_{\text{spring length}}$$

This energy term keeps the atomic polymer intact.

At lower temperature, a greater P is required. Typically a value of $P \sim 20$ is sufficient for aqueous systems at room temperature. It follows that an accurate quantum simulation of many-body systems can be performed in a classical manner, but with a larger classical system composed of "bead" polymers.