Deriving the distribution of *N*-particle kinetic energies in a classical system

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Starting from the Maxwell–Boltzmann distribution of velocities for a single particle, we present a straightforward derivation of the distribution of total kinetic energies for a classical system containing *N* particles. The result is of central importance in the application and design of thermostats in molecular simulations.

Keywords: Canonical distribution; Thermostat; Maxwell–Boltzman; Derivation

Molecular dynamics simulations are often performed at constant temperature, thereby replicating the physical conditions found in the laboratory. For example, in order to correctly sample an ensemble of transition states requires that all relevant molecular configurations can be accessed by the simulation at the temperature of interest. To maintain a constant temperature, however, requires the molecular system to exchange energy with a heat bath [1].

Several algorithms have been developed for this exchange of energy including the Berendsen [2], Nose–Hoover [3–5] and Andersen [6], thermostats amongst others. In order to check the performance of a thermostat in a molecular dynamics simulation, one must verify that the total kinetic energy of the system follows theoretical predictions, namely the canonical distribution. Not only must a thermostat provide the correct average kinetic energy, the fluctuations of the total kinetic energy should also have the proper distribution. As such there has been continual interest in the design of thermostats for molecular simulations. We point out that the Berendsen thermostat, unlike the Nose–Hoover or Andersen thermostats, does not generate the canonical distribution of states. A recent study, however, shows how the Berendsen thermostat can be extended to reproduce the canonical distribution of states [7].

We therefore wish to calculate theoretically the probability density that a classical system of *N* particles has a total kinetic energy of *E*, given that each individual particle has the normal Maxwell–Boltzmann [8,9] distribution of speeds. There is a heuristic derivation by Mandl [10] based upon a dimensional argument as well as a more rigorous derivation noted by Partriaca *et al.* [11,12] which makes use of the formula for the surface area of an *N* dimensional hyper-sphere. In general, however, we found this information difficult to find in the literature. We therefore think it is helpful and interesting to present our straightforward derivation of this distribution here.

For a classical system at a temperature *T*, the probability density that the ith molecule has a translational kinetic energy E_i is given by the familiar Maxwell–Boltzmann distribution

$$P(E_i) = \frac{2}{\sqrt{\pi}} \beta^{3/2} E_i^{1/2}\, e^{-\beta E_i}, \tag{1}$$

where $\beta = 1/k_B T$ and k_B is the Boltzmann factor. For *N* molecules, the probability density that the system has a total kinetic energy *E*, denoted $P_N(E)$, is found by integrating the product $\prod_{i=1}^{N} dE_i p(E_i)$ with respect to all E_i, but ensuring only terms with a total energy of *E* contribute to the integration, *viz.*

$$P_N(E) = \prod_{i=1}^{N} \int_0^\infty dE_i\, p(E_i)\cdot\delta\left(E - \sum_i E_i\right). \tag{2}$$

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The delta function can be expressed as

$$\delta\left(E - \sum_i E_i\right) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{+i\omega\left(E - \sum_i E_i\right)}. \quad (3)$$

Substituting equation (3) into equation (2) gives

$$P_N(E) = \prod_{i=1}^{N}\int_0^{\infty} dE_i p(E_i)\cdot\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{+i\omega\left(E - \sum_i E_i\right)}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{+i\omega E}\left\{\prod_{i=1}^{N}\int_0^{\infty} dE_i p(E_i)e^{-i\omega E_i}\right\}. \quad (4)$$

Using the Maxwell distribution, equation (1), we note that for any particle i

$$\int_0^{\infty} dE_i p(E_i)e^{-i\omega E_i} = \left(\frac{\beta}{\beta + i\omega}\right)^{3/2}. \quad (5)$$

Substituting equation (5) into equation (4) yields the result

$$P_N(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\left(\frac{\beta}{\beta + i\omega}\right)^{3N/2} e^{+i\omega E}. \quad (6)$$

We note that one can arrive at the same result by integrating over momentum space

$$P_N(E) = \frac{1}{Z}\prod_{i=1}^{N}\int_{-\infty}^{\infty} d\boldsymbol{p}_i e^{-\beta\left(\frac{p_i^2}{2m_i}\right)}\cdot\delta\left(E - \sum_{i=1}^{N}\frac{p_i^2}{2m_i}\right), \quad (7)$$

where Z is the normalisation constant

$$Z = \prod_{i=1}^{N}\int_{-\infty}^{\infty} d\boldsymbol{p}_i e^{-\beta\left(\frac{p_i^2}{2m_i}\right)} = \frac{(2\pi)^{3N/2}\prod_{i=1}^{N} m_i^{3/2}}{\beta^{3N/2}}. \quad (8)$$

For even values of N, it is straightforward to calculate the Laurent expansion of the integrand of equation (6) in inverse powers of $(\beta + i\omega)$ and thus obtain.

$$P_{\text{even}N}(E) = \frac{\beta^{3N/2}E^{3N/2-1}e^{-\beta E}}{(3N/2 - 1)!}. \quad (9)$$

We now show that this result holds for all values of N, not just even values. Rather than attempting to evaluate equation (6) directly, let us assume

$$P_N(E) = AE^{3N/2-1}e^{-\beta E}. \quad (10)$$

where A is a constant to be determined. In what follows we set $P_N(E) = 0$ for $E < 0$. The Fourier transform of equation (10) takes the form

$$P_N(\omega) = \int_{-\infty}^{\infty} dE P_N(E)e^{-i\omega E} = A\frac{\Gamma(3N/2)}{(\beta + i\omega)^{3N/2}}, \quad (11)$$

where $\Gamma(3N/2)$ is the gamma function [13]. A comparison of equations (6) and (11) fixes the value of the constant A, and we obtain the final result, valid for all N,

$$P_N(E) = \frac{\beta^{3N/2}}{\Gamma(3N/2)}E^{3N/2-1}e^{-\beta E}. \quad (12)$$

In order to check that a thermostat follows the canonical distribution one must look at the mean kinetic energy as well as the fluctuations about the mean. According to equation (12) the mean kinetic energy is

$$\langle E\rangle = \int_0^{\infty} dE\ E P_N(E) = \frac{3N}{2}k_B T \quad (13)$$

and the deviation in the kinetic energy as a fraction of the mean energy is

$$\frac{\Delta E}{\langle E\rangle} = \frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} = \sqrt{\frac{2}{3N}}. \quad (14)$$

Conclusion

In this article, we have derived a general expression for the distribution of kinetic energies for a classical system of N molecules. Although, this result has previously been documented, we believe that our straightforward derivation is worth noting.

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