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Statistical distribution of bonding distances in a unidimensional solid

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HIGHLIGHTS

- We model a 1D solid using Lennard-Jones potential in Fermi–Pasta–Ulam (FPU) chain.
- We provide the probability distribution for separation distances between particles.
- Numerical simulations agree with the analytical distributions.
- Our theoretical framework supports the argument.

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ABSTRACT

We study a Fermi–Pasta–Ulam-like chain with Lennard-Jones potentials to model a unidimensional solid in contact with heat baths at a given temperature. We formulate an explicit analytical expression for the probability density of bonding distances between neighboring particles, which depends on temperature similarly to the distribution of velocities. For a finite number of particles, its validity is verified with high accuracy through molecular dynamics simulations. We also provide a theoretical framework which is consistent with the numerical findings. We give an analytic expression of the mean bond distance and elastic constant in the case of the square-well and harmonic interparticle potentials: we outline the role played by the hard-core repulsion. We also calculate the same quantities in the case of series expansions of Lennard-Jones potential truncated at different, even series power.

1. Introduction

The unidimensional Fermi–Pasta–Ulam-like systems (FPU, Ref. [1]) are convenient models of solids for both analytical and computational theoretical studies. A broad overview of the subject is available in Refs. [2,3], while its applications can be found in Refs. [4–8]. Recently, in Ref. [9], an FPU-like chain with an open end was shown to mimic closely some thermomechanical properties of real solids, such as thermal expansion and elasticity. Therewith it inspires confidence that modeling thermodynamic properties of solids may be efficiently done by simple means.

We study the one-dimensional chain of point particles, similar to that of Ref. [9], with one or both ends opened to allow for the thermal expansion. We focus mainly on the statistical distribution of individual phase–space variables. For a particle

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in an ideal gas, the normal probability distribution of velocity follows from the Maxwell–Boltzmann statistics, Ref. [10]. The presence of interactions between particles through a potential introduces another form of energy allocation. An interpretation of the same rigor is not available so far for such a general case. However, the Gaussian distribution of velocities is commonly found and thus consistently assumed to hold.

Compared to the ideal gas, where the distribution of spatial coordinates is trivial, the bonding potential energy affects the statistics of configurational degrees of freedom and gives rise to the pair-correlation function. In this paper we investigate with molecular dynamics simulations an FPU-like chain with Lennard-Jones nearest-neighbor interactions, to find a statistical description of the bonding distances between particles, which provide a system of generalized coordinates alternative to the Cartesian. Our main discovery is, that for a finite number of particles there exists some (large) R such that the analytical form for their probability distribution (PDF[r]), which depends on the potential energy U_{LJ} in a way similar to how the distribution of velocities (PDF[$\dot{x}$]) depends on the kinetic energy (K), holds:

$$\begin{cases} \mathrm{PDF}[r] \propto \exp\left(-\dfrac{U_{LJ}(r)}{k_B T}\right)\theta(R-r) \\ \mathrm{PDF}[\dot{x}] \propto \exp\left(-\dfrac{K(\dot{x})}{k_B T}\right) \end{cases} \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature and $\theta(x)$ is the Heaviside step-function.

This is supported by our numerical simulations and analysis of the statistical momenta of the distribution PDF[r]. Further, we provide a theoretical framework, which explains the fact stated in Eq. (1) for the isothermal–isobaric ensemble of point particles in one dimension. The approach is applied for a general inter-particle potential and demonstrated for the cases of the harmonic and square-well interaction. The theoretical framework supports the observations made in the simulations and emphasizes unexpected features emerging from the hard-core repulsion between particles in the harmonic case, e.g. a thermal expansion term. Altogether this identifies the temperature range, within which the classical approach to the FPU problem and ours are practically equivalent, *cf.* Appendix A.

The argument may find its application in calculation of the thermal contributions to the atomic X-ray scattering factor, as was done in a few works in Refs. [11,12]. Since the realistic potentials like that of Lennard-Jones give rise to a PDF, which is not integrable on $rin(0, \infty)$, it is widely believed that the indicated divergence may cause unphysical artifacts Ref. [13].

2. Model

The one dimensional model consists of N point particles of equal masses M arranged on a horizontal line, as sketched in Fig. 1. The particles interact solely with their nearest neighbors through the Lennard-Jones (LJ) potential: $U_{LJ}(r) = E_{LJ}[(r/r_0)^{-12} - 2(r/r_0)^{-6}]$, where r is the bonding distance and E_{LJ} is the minimum of potential well at r_0. The shape of potential is illustrated in Fig. 2 alongside the potentials discussed in Section 5. The particles, indexed in the order of increasing coordinate $x_a < x_{a+1}$, $a = 1..N$, obey the following equation of motion:

$$M\ddot{x}_a = -\frac{\partial U_{LJ}(x_a - x_{a-1})}{\partial x_a} + \frac{\partial U_{LJ}(x_{a+1} - x_a)}{\partial x_a} \tag{2}$$

in the chain bulk.

The right-most particle (i.e. $a = N$) is free and in contact with a deterministic thermostat that operates according to the Nosé–Hoover (NH) scheme at the target kinetic temperature T (Ref. [14]). That is, the equation of motion for the Nth particle together with the evolution of the thermostatting variable χ_R take the form:

$$M\ddot{x}_N = -\frac{\partial U_{LJ}(x_N - x_{N-1})}{\partial x_N} - \chi_R M\dot{x}_N \tag{3}$$

$$\dot{\chi}_R = \left(K_N - \frac{1}{2}k_B T\right) \Big/ \Theta \tag{4}$$

where $K_N = M\dot{x}_N^2/2$ is the kinetic energy of the particle and k_B is the Boltzmann constant; Θ is an adjustable parameter of the thermostat with the characteristic time $\theta = \sqrt{2\Theta/(k_B T)}$.

Analogously, the left-most particle ($a = 1$) is coupled with another NH thermostat. We explore two settings of the boundary conditions at the left end. We refer to the *open* chain, when the first particle interacts via the Lennard-Jones potential also with a fixed wall placed at the origin of the reference frame on the left side. The corresponding equations are:

$$M\ddot{x}_1 = -\frac{\partial U_{LJ}(x_1)}{\partial x_1} - \frac{\partial U_{LJ}(x_2 - x_1)}{\partial x_1} - \chi_L M\dot{x}_1 \tag{5}$$

$$\dot{\chi}_L = \left(K_1 - \frac{1}{2}k_B T\right)/\Theta. \tag{6}$$