Negative specific heat in a Lennard-Jones-like gas with long-range interactions

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Abstract

We study, through molecular dynamics, a conservative two-dimensional Lennard-Jones-like gas (with attractive potential \(\propto r^{-\alpha}\)). We consider the effect of the range index \(\alpha\) of interactions, number of particles, total energy and particle density. We detect negative specific heat when the interactions become long-ranged (\(0 \leq \alpha/d < 1\)).

PACS: 05.20.-y, 05.20.Jj, 64.60.Fr

Keywords: Hamiltonian dynamics; Long-range interactions; Nonextensive statistical mechanics.

Non-Gaussian equilibrium in long-range Hamiltonian systems has recently been reported \([1]\). The authors studied a model of classical planar spins with infinite range interaction, and showed that before going to the Boltzmann-Gibbs equilibrium state, the system reaches a metastable state with a non-Maxwellian distribution of velocities. The duration of this metastable state appears to diverge with the number of particles, i.e., in the thermodynamical limit, the system indefinitely stays trapped in a non-Boltzmann-Gibbs state.

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In this paper, we investigate similar anomalies with a different long-range Hamiltonian model. We consider a two-dimensional gas confined in a box of linear length $L$, defined by the Hamiltonian $H = K + V/\tilde{N} + V_{walls}$, where $K = \sum_{i=1}^{N} p_i^2/(2m)$, the interacting potential is given by $V = \sum_{i<j}^{N} v(r_{ij})$ with $v(r_{ij}) = C \alpha \left[ (\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{\alpha} \right] (0 \leq \alpha < 12)$ and $C = \varepsilon (12^{12/\alpha})^{1/(12-\alpha)}/(12 - \alpha)$. $r_{ij}$ is the distance between the centers of particles $i$ and $j$, $\sigma$ characterizes the diameter of a particle, $m$ is its mass and $\varepsilon$ is the energy scale. We adopt appropriate units in which $\sigma = \varepsilon = m = 1$. $C$ is a factor that makes the depth of the potential well the same $\forall \alpha$. $V_{walls}$ is the repulsive potential of the walls, which assures that the particles are confined within the box. We adopt soft walls, namely $V_{walls} = \sum_{w=1}^{4} \sum_{i=1}^{N} (1/r_{iw})^{12}$, where $w$ is the index for the walls, and $r_{iw}$ is the distance between particle $i$ and wall $w$. The nonextensive scaling parameter $\tilde{N} \equiv 1 + d \int_{1}^{N} \frac{1}{r^d} d r r^{d-1-\alpha}$ (see [3]) is convenient to make the Hamiltonian formally extensive $\forall \alpha/d$ ($d$ is the spatial dimensionality of the system). The model is a variation of the one introduced in [4], and the particular case $\alpha = 6$ recovers the celebrated Lennard-Jones model [5] for dilute nonpolar gases. The variable involved in the range of interactions ($r_{ij}$) is also the dynamical variable, while in the classical spins model, the range of interactions is controlled by the (fixed) position of the particles in the lattice, and not by the angles, which are the dynamical variables. We integrated the equations of motion using the forth order symplectic algorithm [6] with time steps $\Delta t = 0.005-0.02$, which yielded a maximum relative error in the total energy conservation $\Delta E/E \sim 10^{-5}$. We adopted as initial conditions for positions (a) all particles at a triangular lattice (note that this geometry corresponds to the global minimum for a two-dimensional $L^2$ system), and (b) particles randomly distributed, and a water bag distribution for initial velocities. We considered a long-range system with $\alpha/d = 0.5$, and a short-range $\alpha/d = 3$, for comparison.

Fig. [1] shows caloric curves for short- and long-range systems with 100 particles. Each point of the caloric curve is obtained by a time average after a transient of the order of $10^2-10^3$ time units (see Inset), and by an average of a few (up to 10) events with different initial conditions. A negative specific heat region is exhibited for $\alpha/d = 0.5$, while this effect does not appear in the short-range case.

Data collapse in the abscissa of the caloric curve (Fig. [2]) for the long-range case is achieved when the total energy scales as $E/N^{1+x}$, with $x = 0.0876$. 

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Such small value of $x$ is not easily distinguishable (numerically speaking) from a possible logarithmic correction hidden in the power-law scaling introduced by $\tilde{N}$. Such effect was not detected in the classical spins model [1], and could be due to the boundary conditions. Data collapse in the ordinate of the caloric curve may be roughly achieved by scaling the maxima of the curves (for energies below the critical) according to $T_{\text{max}}(N) \sim T_{\text{max}}(\infty) - a/N^y$ ($T \equiv \langle K \rangle / N$) with $y = 0.038$, a value once again very small.

Fig. 3 displays the effect of the particle density in the caloric curve. The negative specific heat region increases with decreasing density, when long-range forces are present. Highly dense systems don’t exhibit such anomaly.

Finally, Fig. 4 shows the probability distribution function (pdf) of velocities for the long-range ($\alpha/d = 0.5$) system, with $N/L^2 = 10^{-3}$ and $E/N = 0.7$ (a state in the negative specific heat region). As $N$ increases, the curves seem to departure from a Maxwellian, exhibiting a slightly positive curvature. A non-Maxwellian pdf was recently found in the classical spins model [1], that might be understood within nonextensive statistical mechanics [3, 7, 8, 9]. Such framework may also be the proper one to handle classical gases with long-range interactions, but only further results would enable a clear conclusion.

We warmly acknowledge the organizers of NEXT 2001 for the general support and hospitality. We also acknowledge CAPES, FAPERJ, CNPq, PRONEX/MCT (Brazilian agencies) for financial support.

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Figure 1: Caloric curves for $N = 100$ and $N/L^2 = 10^{-2}$: $\alpha/d = 3$ (squares), $\alpha/d = 0.5$ (circles). Solid lines are guides to the eyes. Inset: Typical time evolution of $\langle K \rangle / N$. 
Figure 2: Effect of the number of particles in the caloric curve, for the long-range system ($\alpha/d = 0.5$, $N/L^2 = 10^{-2}$). $N = 50, 100, 200, 400$. Inset: the energy per particle at the cusp point as a function of $N$ (log–log scale), slope $x = 0.0876$. 
Figure 3: Effect of the particle density in the caloric curve, for the long-range ($\alpha/d = 0.5$) system with $N = 100$. $N/L^2 = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}$. 
Figure 4: Probability distribution function for the long-range case ($\alpha/d = 0.5$), $E/N = 0.7$ (below the critical energy per particle) and $N/L^2 = 10^{-3}$. $N = 800$, 1600, 2200. We have taken, in the abscissa, the values of both $p_x$ and $p_y$. 

\[ \alpha/d = 0.5 \]
\[ E/N = 0.7 \]
\[ N/L^2 = 10^{-3} \]