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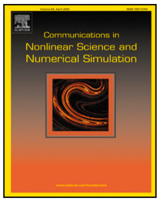

Research paper

On a microscopic equation of state for Lennard-Jones chains

Ruiqi Sun [c,a,1], Lamberto Rondoni [a,b], Federico Frascoli [c,*]

[a] Dipartimento di Scienze Matematiche, Politecnico di Torino, Turin, Italy
[b] INFN Sezione di Torino, Turin, Italy
[c] Department of Mathematics, Faculty of Science, Computing and Emerging Technologies, Swinburne University of Technology, Melbourne, Victoria 3122, Australia

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ABSTRACT

The local thermodynamic equilibrium hypothesis is fundamental to the use of thermodynamic notions and the relations linking them, in equilibrium as well as nonequilibrium states. Its domain of applicability can vary widely across different systems. Monodimensional particle systems often violate the locality condition required by that hypothesis, because correlations can persist over long distances and times. Using a microscopic analogue of the van der Waals equation, which involves the microscopic mechanical equivalent of pressure, temperature and density, we investigate the validity of one of the nonequilibrium relations recently proposed as an equation of state concerning the microscopic mechanical equivalent of temperature and density, for monodimensional chains of particles. We do this without invoking the local equilibrium hypothesis: as we deal with mechanical, not thermodynamic, quantities, we do not need the local equilibrium hypothesis. The origin and validity of such a relation are described and indications are given as to why it works in various regimes of interest. Interestingly, that relation appears to be better satisfied, in our Lennard-Jones systems, when the microscopic "temperature" grows locally or the microscopic "density" decreases. These conditions are respectively favoured by high "temperature" differences at the boundaries, and by increasing the length of the chains. At those state points, that linear relation can be seen as a microscopic analogue of the van der Waals equation we propose. In some cases, a simpler approximation based on that link also exists. These types of relations work quite well for a surprisingly large and physically significant range of nonequilibrium states.

1. Introduction

When macroscopic objects at equilibrium or close to the equilibrium states are considered, thermodynamics is capable of very accurate predictions. With progress in miniaturisation, the discovery of graphene [1] and advancements in nanofabrication [2,3], the last decades have seen the rise of nanotechnology and the emergence of a number of fundamental questions about thermodynamical properties at the nanoscale. So, a growing number of phenomena that pose such questions have been observed [4–9], with one of the most debated being anomalous energy transport and violation of Fourier law, in particular for chains of particles [10–12]. Chains of particles are models often used to represent and investigate structures as different as nanotubes, nanoactuators and nanocantilevers, and are the focus of the present work.

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[*] Corresponding author.
E-mail address: ffrascoli@swin.edu.au (F. Frascoli).

[1] Also at Department of Mathematics, School of Science, Engineering and Computing Technologies, Swinburne University of Technology, Melbourne, Victoria, 3122, Australia.

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In presence of local thermodynamic equilibrium (LTE) [13,14], matter and energy are considered to flow like continua, so that, for instance, the local balances among the observables in the system that lead to Fourier law, at sufficiently small temperature gradients, are justified (consider, for example, Chapter 1 of Ref. [14]). In that case, one finds that the heat flux along a macroscopic rod is inversely proportional to its length, if the temperatures at the two ends are maintained constant. Similarly, chains of particles can be seen as approximations to rods contracted to one-dimensional objects, but the same inverse proportionality between flux and density does not necessarily hold, showing that LTE and consequently Fourier law might not apply.

Understanding the properties of one dimensional systems is the driver of this paper, in the light of one equation that has been proposed and verified for one-dimensional chains [15–18]. The validity of that relation is independent from LTE and expresses a linear dependence of the time averaged kinetic energy of a single particle in a chain of oscillators on the time averaged distance of two consecutive particles in the chain. Such quantities can be seen, respectively, as single particle analogues of the local temperature and of the inverse of the local density, as indeed in equilibrium they can be identified with those thermodynamic properties. It is important, though, to immediately stress that they refer to individual particles and are not equivalent to thermodynamical definitions. The relation is given as:

$$T_i = \alpha_1 \rho_i^{-1} - \alpha_2. \tag{1}$$

with α_1 and α_2 being constant coefficients, T_i the average kinetic energy of particle i, ρ_i^{-1} the average of the single particle inverse density.

The relation above, proposed in Ref. [19], could lead to a type of single particle and nonequilibrium pressure–density–temperature state equation for monodimensional nanoscopic systems, reminiscent of the linear Charles's law (see, for example, Section 1 A.2 of Ref. [20]). This means that, in a monodimensional chain, the single particle "temperatures" T_i, are linearly related to the inverse, single particle "local densities" ρ_i^{-1}, i.e. the differences in the mean positions of consecutive particles $(x_{i+1} - x_i)$. This relation is based on the idea that, in macroscopic systems, energy equipartition relates the thermodynamic equilibrium temperature to a time average of the kinetic energy of a single particle and is equal to a number of other microscopic quantities [4,21–23]. On the other hand, Eq. (1) has a nature that is very different than that of a thermodynamic equation of state in nonequilibrium systems, because local thermodynamic quantities pertain to practically isolated mesoscopic cells, containing a large number of particles in equilibrium [15,18,21,24–28]. We also stress that Eq. (1) does not refer to the mechanical analogue of pressure, which is momentum exchange. Naturally, there is such an exchange of momentum at the ends of the chain, that corresponds to a given state of the system. But the state, as usual, is determined by only two (out of three) variables.

In this paper, we investigate a possible explanation for the origin and applicability of the linear relation Eq. (1), introducing a single particle version of the van der Waals (mvdW) equation for real gases that, to the best of our knowledge, has never been used before. Note that, here and in the rest of this work, "linear" is used in terms of functional dependence, e.g. linear as opposed to quadratic or exponential for example, and is never intended as referring to linear response theory. The van der Waals formulation is not microscopic, applies to equilibrium only and, to the very least, requires averaging over mesoscopic cells. In this work, instead, we present a single particle version of the equation that is related to the linear relation (1). Using chains of N Lennard-Jones (LJ) oscillators without on-site potentials, as given in a number of references in the literature [15,18,21,24–27,29], we investigate the behaviour of temperature and pressure and find which equilibrium properties extend to nonequilibrium when a temperature gradient is applied. The rationale behind choosing the mvdW formulation is that, besides its ability to describe gaseous behaviour in macroscopic systems, the van der Waals equation can also be obtained as a mean field approximation (Section 5.3 of Ref. [30]) and can thus be applied to macroscopic systems with microscopic, short range interactions, like those described by the LJ potential. With this approach, (a) the linear relation can be seen as a state equation for steady state of a "gaseous-like" phase for nonequilibrium one-dimensional chains, which appears when temperatures on both ends are high or when temperature gradients are sufficiently high; (b) in some circumstances it can be seen as a good approximation of the mvdW equation; (c) coefficients in such relation are generally a linear function of overall, steady-state pressure in the system and not individual local densities, but (d) the relation's applicability at low temperature and high density becomes more problematic. Finally, (e) these results appear to be robust and independent from the chain length when appropriate temperature jumps are considered.

The paper is organised as follows. Section 2 describes monodimensional chains with LJ potentials and explains the formulae we will use, Section 3 uses the mvdW equation to prove the properties of monodimensional chains in equilibrium and then discusses the validity of Eq. (1) to nonequilibrium steady states in the light of its relation to mvdW equation. The last Section is devoted to the conclusions and final remarks about future works.

2. Details of the model

For our investigation, as sketched in Fig. 1, the system we consider is a monodimensional chain of N identical moving particles, with the same masses m and positions denoted by $x_1, ..., x_N$. Two particles are fixed at the ends, at $x_0 = 0$ and $x_{N+1} = L$, where L is the total length of the chain. Interactions only exist among nearest neighbours, via a LJ potential:

$$V(r) = \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^{6} \right], \tag{2}$$

where r is the distance between nearest neighbours: $r = |x_{i+1} - x_i|, i = 0, 1, \dots, N$, and $\epsilon > 0$ is the depth of the potential well. When $r = \sigma$, the potential $V(r)$ has a minimum, thus $x_i = i\sigma$ with $i = 0, \dots, N+1$ is a configuration of stable mechanical equilibrium. In that case, $L = (N+1)\sigma$ is the equilibrium length of the whole chain. As a consequence of the repelling part of the potential, the order of particles (e.g., $0 < x_1 < x_2 < \cdots x_N < L$) holds at all times, provided it does at the initial time $t = 0$.

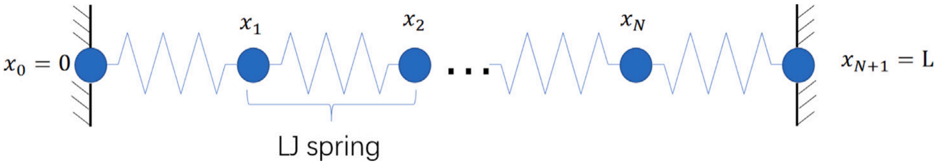


Fig. 1. Sketch of the chain of particles, with reciprocal Lennard-Jones interaction, that are considered in this work.

Besides the force exerted by nearest neighbour particles, the first and the last particle in the chain are also subject to two separate Nosé–Hoover (NH) thermostats, at kinetic temperature T_L (on the left of the chain, particle 1) and T_R (on the right of the chain, particle N), with relaxation times θ_L and θ_R. The thermostats act on particles 1 and N with a force given by

$$F_{NH}(x_i) = -\xi_i \dot{x}_i \qquad i = 1,\ N \tag{3}$$

where ξ is a multiplier that depends on the target temperatures T_L or T_R. The following $2N+2$ equations of motion thus hold, overall:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = v_i \qquad i = 1, \dots, N \tag{4}$$

$$\frac{\mathrm{d}v_i}{\mathrm{d}t} = F(x_i - x_{i-1}) - F(x_{i+1} - x_i) \qquad i = 2, \dots, N-1 \tag{5}$$

$$\frac{\mathrm{d}v_1}{\mathrm{d}t} = F(x_1 - x_0) - F(x_2 - x_1) - \xi_1 v_1 \tag{6}$$

$$\frac{\mathrm{d}v_N}{\mathrm{d}t} = F(x_N - x_{N-1}) - F(x_{N+1} - x_N) - \xi_N v_N \tag{7}$$

$$\dot{\xi}_1 = \frac{1}{{\theta_L}^2}\left(\frac{m{v_1}^2}{k_B T_L} - 1\right) \; ; \quad \dot{\xi}_N = \frac{1}{{\theta_R}^2}\left(\frac{m{v_N}^2}{k_B T_R} - 1\right) \tag{8}$$

with the last two terms representing the equations for the constraints of the NH thermostats. Fixed boundary conditions at the beginning and at the end of the chain, $x_0 = 0, x_{N+1} = L$, are imposed at all times t. As a consequence, the density of the chain (i.e., the average density of particles on the chain) is given by:

$$\rho = \frac{N+1}{L}. \tag{9}$$

Denoting time averages with angular brackets, $\langle \cdot \rangle$, one of the observables we consider is the single particle "pressure" P, defined by the average of the force F between any two nearest neighbours. When the chain is in a stationary state, note that the following homogeneity condition holds:

$$P = \langle F(x_2 - x_1) \rangle = \langle F(x_3 - x_2) \rangle = \cdots = \langle F(x_N - x_{N-1}) \rangle . \tag{10}$$

Unlike P, the single particle density ρ_i is defined by

$$\rho_i = \frac{1}{\left\langle x_{i+1} - x_i \right\rangle}. \tag{11}$$

For a particle i, ρ_i varies in space, in general, because particles move away from their equilibrium positions when the thermostats are set at different temperatures, $T_L \neq T_R$.

Finally, we denote the kinetic single particle temperature by:

$$T_i = \frac{m}{2}\langle {v_i}^2 \rangle. \tag{12}$$

Note that all the units are assumed to be reduced from now on, with the Boltzmann constant k_B set to unity. In the following, we numerically integrate Eqs. (4)–(8) via a fourth-order Runge–Kutta method with step size 10^{-3}. Time averages are typically taken over the interval $[1 \cdot 10^7, 4 \cdot 10^7]$, except in the cases we explicitly identify. Also, the number of particles we consider in this work is fixed at $N = 1000$, except for explicitly noted cases when the N dependence of results is discussed. All the parameters for the LJ potential are set to unity, $\epsilon = 1$ and $\sigma = 1$. The mass of every particle is also set at unity, as well as the relaxation times of the thermostats, i.e. $m = \theta_L = \theta_R = 1$. The boundary temperature T_L, T_R will be set at equal or unequal values, depending on whether the system is studied at equilibrium or out of equilibrium, respectively. Chain densities will also be varied, adjusting the length L of the chain and maintaining the range of ρ within the reduced interval $(0, 1]$.

3. Results and discussion

3.1. The equilibrium case

Firstly, let us consider the case of a LJ chain at equilibrium. Our goal is to compare the behaviour of the chains with the mvdW equation and see in which regimes the agreement is valid and why. According to thermodynamics, the equilibrium state of a given mass in a single phase can be represented by a function of two thermodynamic variables [31] and the others can be inferred from the two chosen ones. An equilibrium state, for example, can be described by a function of temperature and density, where it is understood that the corresponding quantities are averaged over many particles and over sufficiently long times. For the system considered in this work, which is monodimensional and made of particles of a single species and with unitary mass, we stress again that we conjecture that the same conclusion should hold, even away from equilibrium and for single particle quantities, without averaging over many particles. Moreover, if the thermostats are at the same temperature $T_L = T_R$ and the average density is ρ for a chain of length L, the value of the pressure should be written as a function of global quantities T and ρ, e.g. $P = P(T, \rho)$. Hence, let us consider the dependence of pressure on ρ at constant T, and compare it with the prediction made by the mvdW equation, given, for our system, by:

$$(P + a\rho^2)(1 - \rho b) = \rho T, \tag{13}$$

where we take $R = 1$, expressing the various quantities in reduced units. The mvdW Equation is thus written as the standard vdW Equation but applied to single particles in the LJ chain. Then, we can use P/ρ as dependent variable and rewrite everything as

$$\frac{P}{\rho} = \frac{T}{1 - b\rho} - a\rho, \tag{14}$$

with the two undetermined coefficients (a, b) that, as it is well-known, in the typical context where this equation is used depend on the characteristics of the gas we consider. Similarly, for LJ chains, we assume that they will depend on the characteristics of the chains.

We are interested in seeing how well the mvdW Equation can justify the relations between observables (ρ, P, T) in our system. We find that this Equation is not adequate to describe the behaviour of equilibrium chains at low temperature (see Fig. 2(a)–(b)), as the ratio between pressure and density does not seem to change sensitively with density. This prevents the mvdW from being a good model for the linear chain, which is in a state that does not resemble a standard gaseous phase. As T rises, the mvdW equation becomes a good model of the chain's behaviour, as can be seen in panels (c) and (d) in Fig. 2. Note that this is a new representation of the single particle properties, not directly related to the spatial dependence of the variables treated by Eq. (1). While at equilibrium this makes no difference, away from equilibrium it provides a different perspective on single particle quantities. The mvdW equation is a very good predictor of chain's observables as the temperature is increased to values such as $T_L = T_R = 0.5$, as shown in Fig. 3(a). This agreement is maintained throughout every higher temperature we have considered, as shown in the remaining panels of the Figure, with an improvement for higher densities as T increases. It is interesting to note that, at high temperatures, a simplified relation describes the chain's behaviour as well as the mvdW Equation does. Indeed, the term $a\rho$ becomes smaller than the rest, with a assuming an almost constant value of $a \approx 0.5$. Also, when fitted to the mvdW curves, b remains practically constant and close to the value of the potential constant $\sigma = 1$ throughout the spectrum of temperatures we simulate, with $b \approx 0.82$. A simpler relation for high T's can be written as:

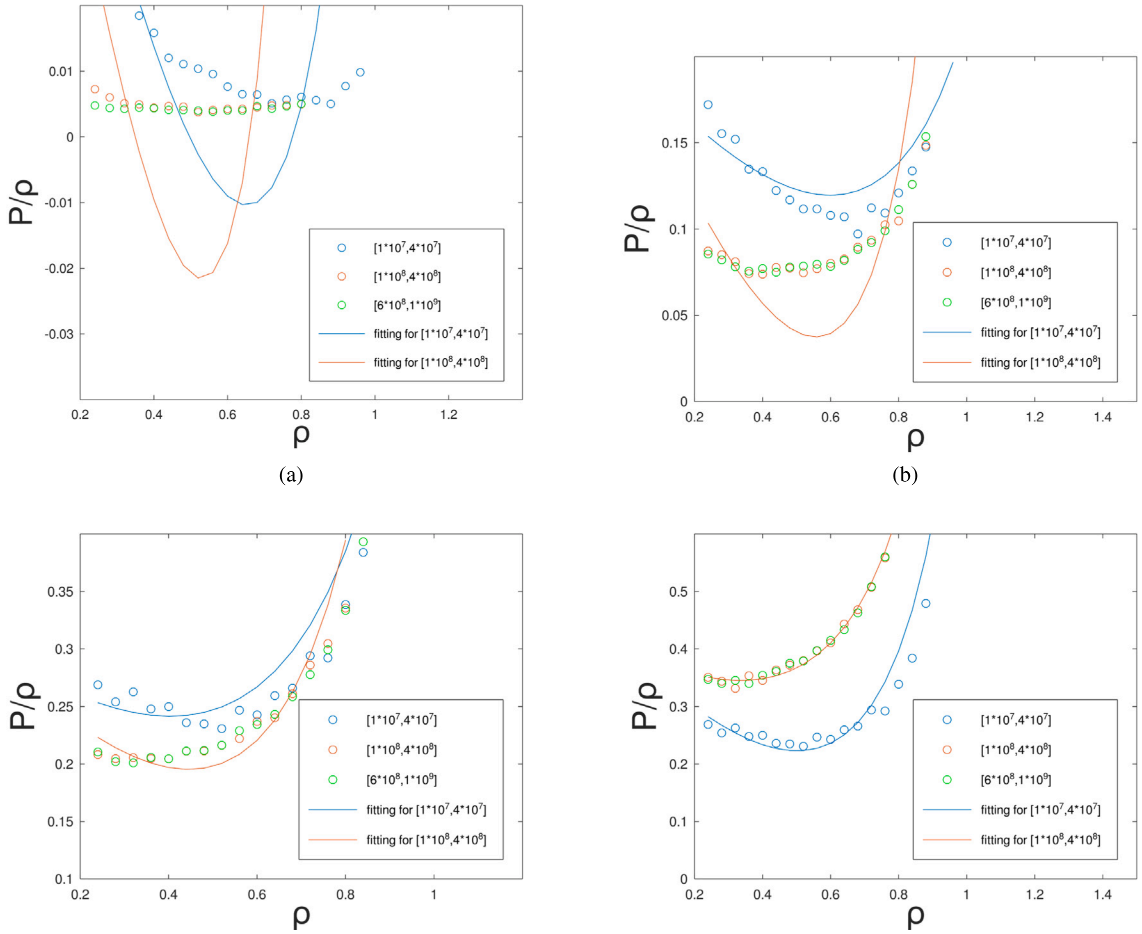
$$P/\rho = \frac{T}{1 - \rho b}, \tag{15}$$

which works well in predicting P/ρ for sufficiently high temperatures, as illustrated in the panels in Fig. 3. The formula can be also justified using physical arguments, as follows.

Suppose that there are N particles confined on a straight line of length L and at equilibrium at temperature T. The average exchanged momentum between particles must be approximately proportional to the square root of temperature, given that $T =< p^2/(2\ m) >$. Note that the particles are still on average, in the steady state, and the average exchanged momentum is the average of the absolute value of p. If we consider that the pressure experienced across the line of particles is the product of exchanged momentum with the frequency of collisions, we can arrive at Eq. (15) as follows. Suppose the mean free length of the chain is expressed by $(L - Nb)/N$, where we have excluded from the total length the N particles, all supposed to be hard and of diameter b each (somehow analogue to the meaning of b for the macroscopic vdW formulation). In this case, $(L - Nb)/N = \rho^{-1} - b$, which we can divide by the mean exchanged momentum to get the mean free time between collisions as $(\rho^{-1} - b)/\sqrt{2Tm}$. If we invert this expression, we obtain the average frequency of collisions per mass. We can then multiply it by the exchanged momentum, which, as said, is proportional to $\sqrt{2Tm}$, and arrive at an approximation for the pressure as

$$P \ \propto \ \frac{T}{\rho^{-1} - b}.$$

If solved for T, this relation gives an expression in line with Eq. (15). As a matter of fact, the LJ particles tend to behave like hard-core particles when the system is at equilibrium and at a high temperature. So, at equilibrium, it seems reasonable to conclude that the mvdW equation correctly captures one dimensional systems when temperature is sufficiently high.



(a) (b)

(c) (d)

Fig. 2. An example of four profiles for P/ρ versus ρ as per Eq. (14), at increasing but low temperatures. (a) At $T_L = T_R = 0.1$ the mvdW equation fails everywhere due to the low temperature regime, but as the temperature is risen to (b) $T_L = T_R = 0.2$, (c) $T_L = T_R = 0.3$ and (d) $T_L = T_R = 0.4$ the agreement gradually improves and becomes almost complete, except for very low densities. Note that the time intervals chosen for thermalization show that the system reaches a steady state around $t \approx 10^8$, since results do not change significantly for larger times, except for very low densities.

3.2. The nonequilibrium case

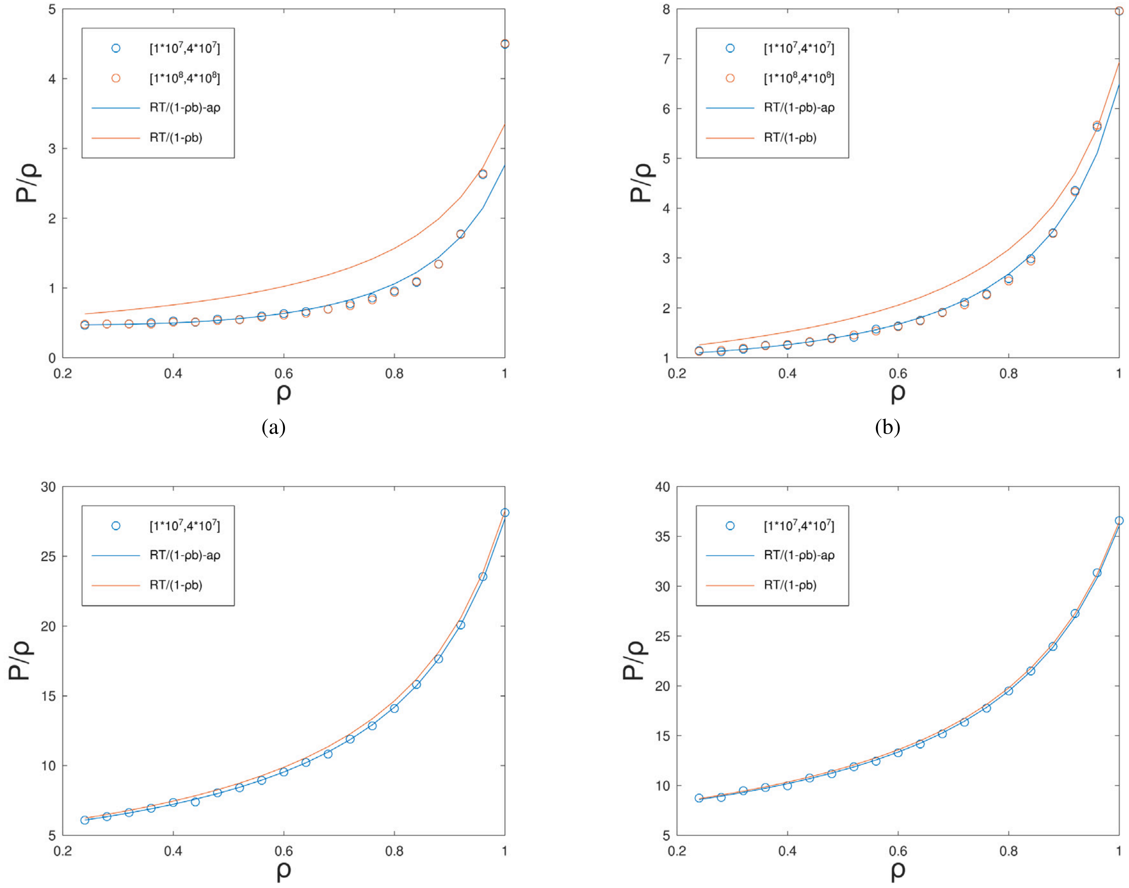
Let us now move to the case where the LJ single chain is not at equilibrium, because $T_L \neq T_R$. Previous arguments used for $T_L = T_R$ about chain average density, exchanged momentum and frequency of collisions do not hold anymore and we need to look at the dependency of the local temperature on pressure and local density, where for "local" we remind the reader that we mean "per single particle". Since pressure P is still a constant at the steady state, we use the mvdW equation and apply it per particle, invert for T_i and obtain a relation for the temperature of each chain component i as a function of P and particle density ρ_i:

$$T_i = P\rho_i^{-1} - Pb + a(\rho_i - b\rho_i^2) \tag{16}$$

This expression contains a linear (first order) term in pressure, i.e. $P\rho_i^{-1} - Pb$, which is Eq. (15), and a nonlinear (higher order) term in particle positions, e.g. $a(\rho_i - b\rho_i^2)$, that acts as a correction to the equilibrium case. To compare this expression with the linear relation Eq. (1), we observe that Eq. (16) can be seen as a function of the system variables, as follows:

$$\begin{aligned} T_i &= C_1(T_L, T_R, P(T_L, T_R, \rho)) \cdot \rho_i{}^{-1} + C_2(T_L, T_R, P(T_L, T_R, \rho)) \\ &= C_1(T_L, T_R, \rho) \cdot \rho_i{}^{-1} + C_2(T_L, T_R, \rho), \end{aligned} \tag{17}$$

where parameters C_1 and C_2 are now assumed to be functions of boundary temperature T_L, T_R and pressure P, as they are in Eq. (1). Since the pressure itself could be understood as a function of T_L, T_R and average density ρ, the two parameters C and the whole



(a) (b)

(c) (d)

Fig. 3. Example of four profiles for P/ρ versus ρ at equilibrium, as per Eq. (14), at moderate to high temperatures. (a) At $T_L = T_R = 0.5$, the mvdW equation works quite well for almost every density considered, except for high ones. The accuracy increases for higher temperatures such as (b) $T_L = T_R = 1.0$, and the data are perfectly fit for higher temperatures (c) $T_L = T_R = 5.0$ and (d) $T_L = T_R = 7.0$. The approximation in Eq. (15) increases its accuracy as temperature increases and is generally an overestimation of the actual data for average temperatures, as shown in panels (a) and (b).

linear relation (17) could be taken as functions of only the average density ρ when T_L, T_R are given. So, we can provide the range of validity of Eq. (15) and consider when the mvdW and that relation agree with simulation data.

Our simulations demonstrate that relation (1), now also seen as one way of expressing the mvdW Eq. (16), does not apply for certain choices of the boundary temperatures T_R and T_L. To reveal the nature of this failure, we choose to fit Eq. (1) optimising the fit for the part of the chain at higher per particle temperature T_i, following another approach with respect to the one used to assess Eq. (1) in its original formulation. Then, we find that Eq. (1) is not verified, since the curve deviates from the linear relation Eq. (1) on the left of the vertical lines in the plots of Fig. 4.

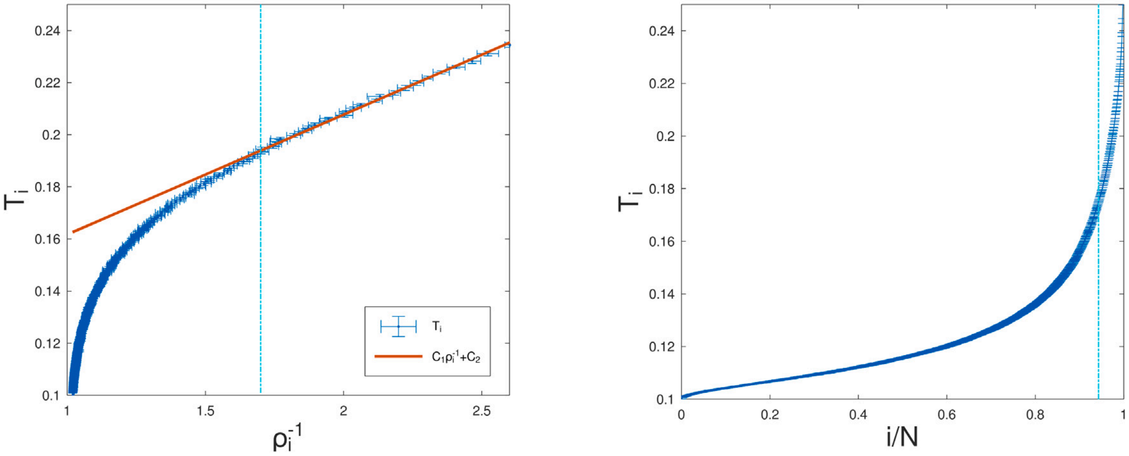
To further stress that the mdvW Equation and Eq. (1) cannot be straightforwardly related to each other in this regime, higher order terms in the local density can be considered for the latter as a form of virial expansion, and we can write

$$T_i = P\rho_i^{-1} + M_0 + M_1\rho_i + M_2\rho_i^2 \tag{18}$$

in which P is the pressure, and the three coefficients M_0, M_1, M_2 are independent of each other. Even if these coefficients, once appropriately fitted, can describe the chain behaviour appropriately, they cannot be predicted or justified using the mvdW Equation. In fact, if we compare the equation above with the relation from mvdW in Eq. (16), we find that $M_0 = -bP$, $M_1 = a$, $M_2 = -ab$, giving the relation

$$\frac{M_0 M_1}{M_2} = P \tag{19}$$

Using the correct $P = 0.0425$, which has been extracted from the simulation data using Eq. (10), there is a contradiction between the results obtained by fitting Eq. (18) to Fig. 4(a) (not shown), which provides the values $M_0 = -7.5682, M_1 = 13.903, M_2 = -6.2967$.



(a) (b)

Fig. 4. (a) Per particle temperature T_i with respect to inverse local density ${\rho_i}^{-1}$, with errors being obtained by ensemble averaging of 10 different initial states, each one over the time interval $[1 \cdot 10^8, 1 \cdot 10^9]$. The linear fit is obtained by using Eq. (1) (orange line) and optimised for higher local temperatures T_i. (b) The corresponding temperature profile for $N = 1,000$ particles, where i indicates particle number along the chain, with 1 being the leftmost and 1,000 being the rightmost. Having chosen to fit Eq. (1), or equivalently Eq. (17), with the data on the right of the two panels, the curves at the right of the vertical blue line represent the particles in the chain that give rise to the linear regime. This behaviour is typical of the system and the choice of fitting. For both panels, uncertainty is given as twice the standard deviation. Note that, for both plots, the first five particles from the left and the last five particles from the right in the chain are not considered.

According to Eq. (19), this would imply that the pressure for the system at $T_L = 0.1, T_R = 0.3, \rho = 0.9$ should be as high as 16.71, which is way off the observed data.

On the contrary, the linear relation (1) works and can be derived using the mvdW equation, which also works, if one considers high temperatures or low densities. Decreasing the average density ρ, which can be obtained by elongating the chain at a fixed number of particles N, Figure 5(a) shows that the linear region extends to lower T_i and its start is pushed towards the left side of the graph. Note that data is normalised in the following way: first, re-scale ρ_i^{-1} and T_i to the range $(0, 1]$ by

$$\rho_i^{-1} = \frac{\rho_i^{-1} - \min(\rho_i^{-1})}{\max(\rho_i^{-1}) - \min(\rho_i^{-1})}$$

$$T_i^{-1} = \frac{T_i - \min(T_i)}{\max(T_i) - \min(T_i)}$$

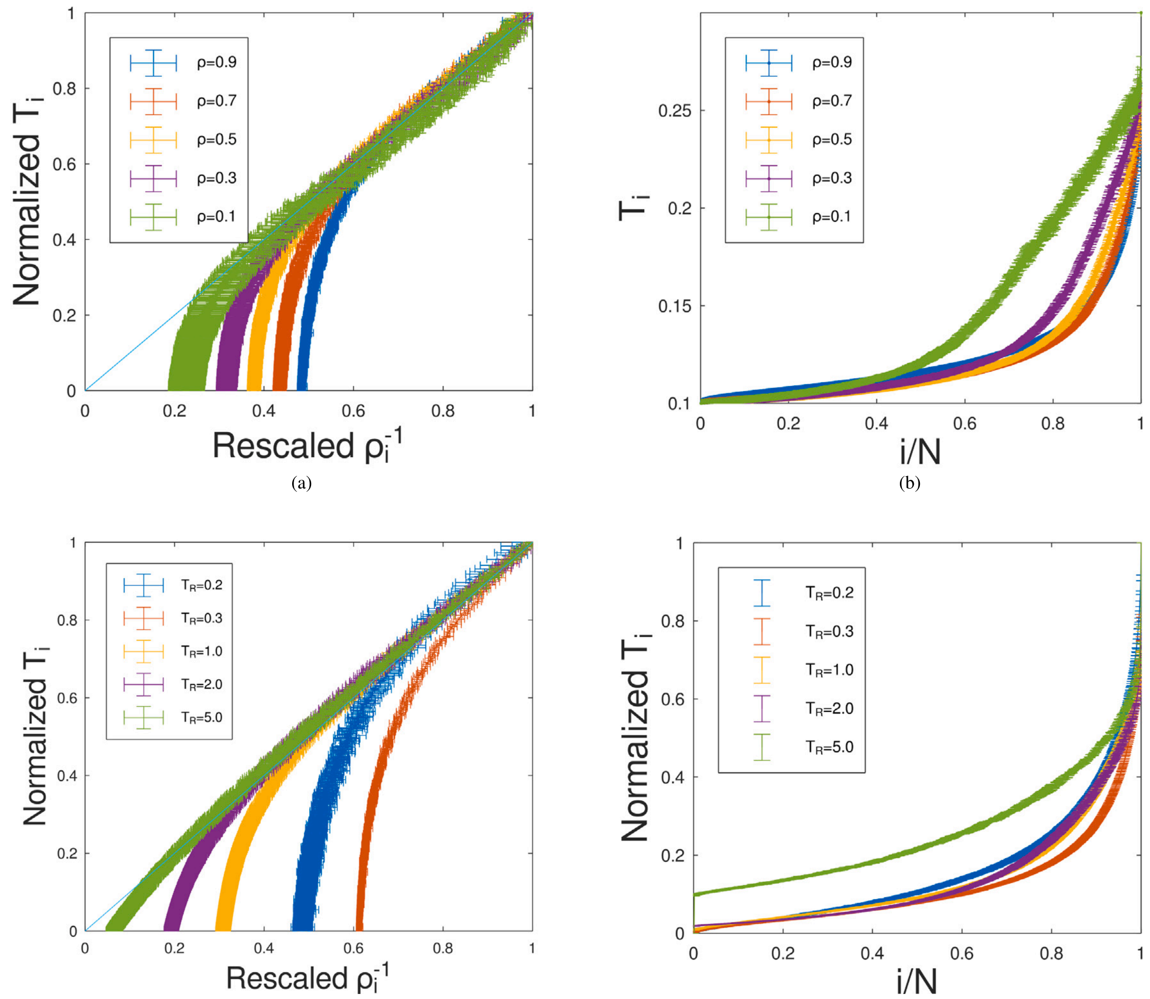
and then employ a transformation to normalise the slope of the linear region:

$$\rho_i^{-1} = 1 - (1 - \rho_i^{-1}) C_1 \frac{\max(\rho_i^{-1}) - \min(\rho_i^{-1})}{\max(T_i) - \min(T_i)}.$$

Note also how the per particle temperature in Fig. 5(b) changes accordingly. As expected, a similar effect can also be obtained by an increase in the temperature in the system, something that can be reached even by increasing only one of the baths' temperatures. It is interesting to note that this takes the system further away from equilibrium, which proves once more that our microscopic equations of state are not of thermodynamic nature (see Fig. 5(c)–(d)). The non-linearity decreases gradually as T_R increases and concentrates at the lower end of the local T and local ρ^{-1} (e.g. close to the origin of the plot). It is interesting to point out that the profile for the case $T_R = 0.2$ shows a more extended linear regime than $T_R = 0.3$ (compare the blue and red profiles in Fig. 5(c)). The extension of the region where linearity holds may not be monotonic with $(T_R - T_L)$ and could be irregular for relatively small temperature jumps across the chains. For very large gradients such as those with $T_R = 5.0$ instead, the local density in the chain shows a clear change in its curvature (see panel (d)) and the linear relation (1) is accurately verified.

According to the discussion above and based on what we have shown for the mdvW equation, we conclude that the linear relation works for nonequilibrium LJ chains at low density and high temperature, which also corresponds to the regime where the mvdW equation works well. In particular, these regimes are practically the same as those at equilibrium with values of $T_L = T_R$ and ρ when the mvdW equation works. So: if the relation works at equilibrium for the highest temperature T_R and the jump $(T_R - T_L)$ is sufficiently large, the relation will work at nonequilibrium. If the temperature T_R is large and $(T_R - T_L)$ is not large, then it is similar to an equilibrium state with $T_L = T_R$ large, and it will work well since the relation works well for equilibrium at T_R large. The question that remains to be addressed is the following: what is the relation between Eqs. (16) and (17) in the regimes when they both hold at nonequilibrium? Eq. (17) directly derives from the mvdW Eq. (16), and coefficients C_1 and C_2 are given by

$$C_1 = P \tag{20}$$



(a) (b)

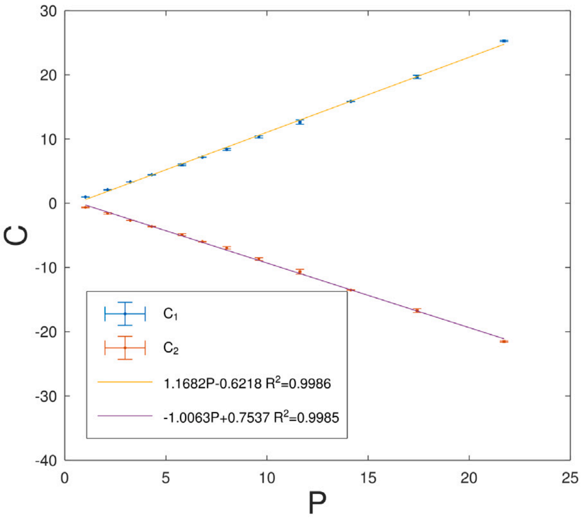
(c) (d)

Fig. 5. (a) Using a low temperature jump $T_L = 0.1, T_R = 0.3$, the linear relation (1) is tested for decreasing $\rho = 0.9, 0.7, 0.5, 0.3, 0.1$. All data is obtained by ensemble averages of 10 different initial states over the time interval $[1 \cdot 10^8, 1 \cdot 10^9]$. (b) The corresponding per particle temperature T_i profiles. Note how, as the chains increasingly verify the linear relation, the profiles shift towards the left as ρ decreases. (c) Using a constant $\rho = 0.9$, larger temperature jumps are considered, for a fixed $T_L = 0.1$ and a varying $T_R = 0.2, 0.3, 1.0, 2.0, 5.0$. All data is again obtained by ensemble averages of 10 different initial states over times $[1 \cdot 10^8, 1 \cdot 10^9]$, except when $T_R = 5.0$, where three initial states being run for $[1 \cdot 10^7, 4 \cdot 10^7]$ are considered. (d) The corresponding T_i profiles. Note how $T_R = 5.0$ shows a different "temperature" profile, with higher T_i for low i. For all panels, uncertainty is given as twice the standard deviation and the five particles closer to the right and left edge of the chains are not considered.

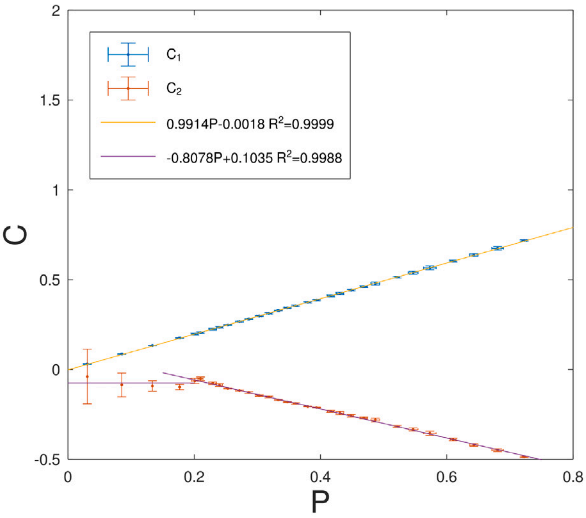
$$C_2 = -Pb \tag{21}$$

Note that with constant boundary temperature T_L, T_R, both C_1 and C_2 are functions of the steady state pressure P only, or equivalently, functions of average density (see Eq. (17)), and this allows us to compare the behaviour of C_1 and C_2 at different regimes. As Fig. 6 clearly shows, the agreement across various pressures (and densities) is impeccable, except for the cases at very low pressure. This is due to the higher order terms in Eq. (16), i.e. $a(\rho_i - b\rho_i^2)$, which become particularly significant when pressure is low. See, for instance, how C_1 increases linearly and C_2 plateaus when $P \lessapprox 0.2$: this occurs because, for P approaching zero, C_2 must be negative (see Eq. (21)).

Finally, we remark that the results we have shown are not dependant on the length of the chain: in Fig. 7(a)–(b), a collection of results for chains with increasing number of particles is shown, considering different temperature jumps. Eq. (1) is valid across the whole range of chains we tested and the slope of the line is practically constant, once the difference between T_L and T_R is chosen.



(a)high pressure



(b)low pressure

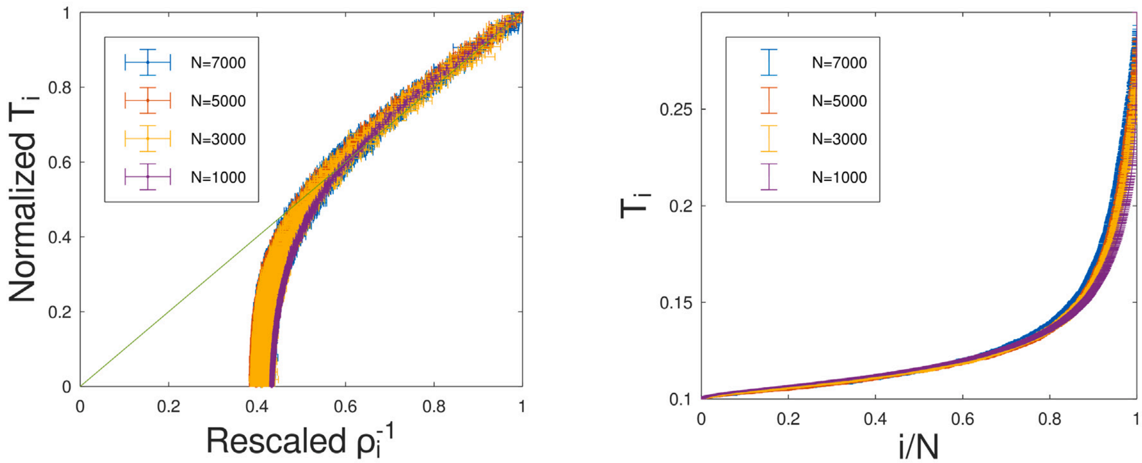
Fig. 6. C_1 and C_2 as functions of pressure P, at steady state and for different average densities of the chains. In both plots, the agreement is significant, except for C_2 in panel (b). Note that we use a range of densities (and hence pressures) to show that the linear relation is robust across different regimes. Note how uncertainty in C_2 increases as P is closer to zero: C_2 seems unlikely to be linear with pressure, because it cannot be positive, according to Eq. (21), and likely saturates close to zero.

4. Conclusions

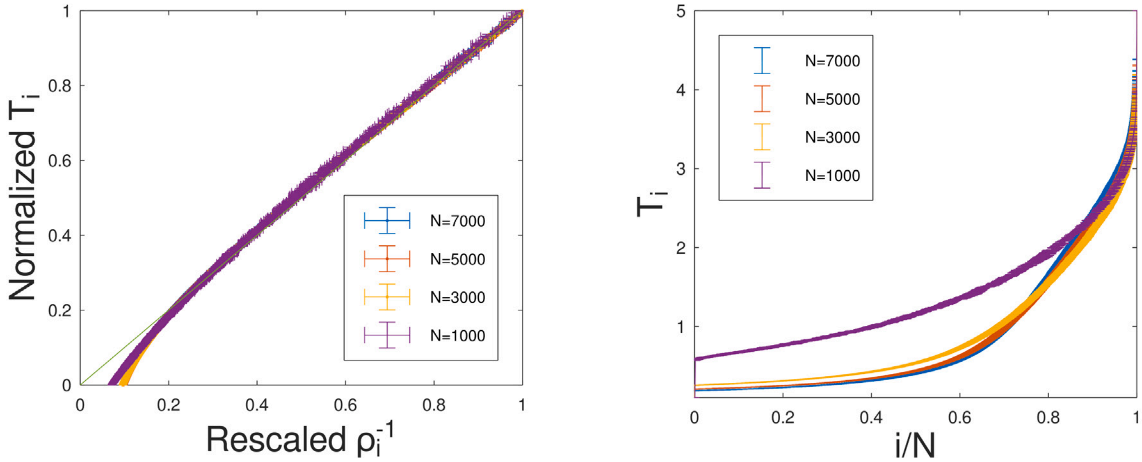
In this work, we have presented a series of theoretical and numerical results on monodimensional chains of particles, interacting via a Lennard-Jones potential and in contact with two Nosé–Hoover thermal baths at the chain's extremities. Using the proposed, per particle mvdW equation and the linear relation Eq. (1) between per particle temperature and inverse density, we conclude that the two equations are equivalent for a large range of states and fail for specific thermodynamical regimes.

When low temperatures are imposed on both ends, the linear relation is not very accurately verified. In that case, its relation to the mvdW formulation is unclear and the mvdW equation cannot be applied. When one of the thermal baths is set at high temperature, a high temperature is established in good part of the chain, and the linear relation works better and better as the temperature increases.

The parameters of the linear relation vary linearly with pressure, as suggested by the form (16) of the mvdW equation, from which the linear relation is immediately derived as Eq. (17). Also, the validity of the linear relation does not seem to depend on



(a)low $(T_L - T_R)$ (b)low $(T_L - T_R)$



(c)high $(T_L - T_R)$ (d)high $(T_L - T_R)$

Fig. 7. Relation between T_i and ρ_i^{-1}, computed for chains of lengths $N = 1000, 3000, 5000, 7000$ at a density $\rho = 0.9$. The temperature at the end is kept constant at $T_L = 0.1$, $T_R = 0.3$ for panels (a)–(b) and it is at $T_L = 0.1$, $T_R = 5.0$ for panels (c)–(d). Uncertainty is calculated as twice the standard deviation for 10 independent runs. Eq. (1) gives similar results for α_1 for panel (a), with values $\alpha_1 = 0.051$ for $N = 1000$, $\alpha_1 = 0.046$ for $N = 3000$, $\alpha_1 = 0.046$ for $N = 5000$ and $\alpha_1 = 0.050$ for $N = 7000$, respectively. Linear regimes all start at a similar value of ρ^{-1}. Results for panel (c) are analogous, with a more extended linear regime. Panels (b) and (d) show the dependance of local T_i on particle positions along the chain. Similar effects as the previous Fig. 5 are present.

either the number of particles in the chain. All of these findings suggest that the linear expression firstly introduced in Ref. [19] can be regarded as a *local, i.e.* per particle, state equation for nonequilibrium monodimensional LJ chains in a wide range of kinetic temperatures and of densities.

Furthermore and as an interesting follow-up from the present work, we will investigate the case with constant confining forces acting at the two ends of the chain, rather than constant chain length determined by the position of the first and last fixed particles. This will allow us to understand the possible dependence of the validity of Eq. (1) on the boundary conditions.

In conclusion, it is important to stress that our relations only formally resemble thermodynamic state equations, while their nature is totally different. In the first place, they apply to single particle properties, rather than collective properties of large numbers of particles constituting mesoscopic cells. They apparently apply arbitrarily far from equilibrium and, given their independence from local equilibrium, they also work in cases in which the LTE condition may not be satisfied. Note that, in our system, local equilibrium seems to be violated by the fact that boundary effects are not negligible even in the centre of the chain, especially for large differences in temperatures between T_L and T_R.

Future research is under way to clarify the mechanisms leading to the validity of the single particle state equations, and their dependence on both the microscopic dynamics and their thermodynamic counterparts.

CRediT authorship contribution statement

Ruiqi Sun: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Lamberto Rondoni:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Federico Frascoli:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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