A one-dimensional hard-point gas and thermoelectric efficiency

J. Stat. Mech. (2009) L03004

(http://iopscience.iop.org/1742-5468/2009/03/L03004)

Journal of Statistical Mechanics: Theory and Experiment
An IOP and SISSA journal

LETTER

A one-dimensional hard-point gas and thermoelectric efficiency

Giulio Casati[1,2], **Lei Wang**[3,4] **and Tomaž Prosen**[5]

[1] Center for Nonlinear and Complex Systems, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy
[2] CNISM, CNR-INFM, and Istituto Nazionale di Fisica Nucleare, Sezione di Milano, Italy
[3] Department of Physics, Renmin University of China, Beijing 100872, People's Republic of China
[4] Department of Physics and Center for Computational Science and Engineering, National University of Singapore, 117542, Singapore
[5] Physics Department, Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia
E-mail: giulio.casati@uninsubria.it, phywangl@nus.edu.sg and tomaz.prosen@fmf.uni-lj.si

Received 15 December 2008
Accepted 2 March 2009
Published 25 March 2009

Online at stacks.iop.org/JSTAT/2009/L03004
doi:10.1088/1742-5468/2009/03/L03004

Abstract. We study heat and particle transport in a classical disordered, one-dimensional, hard-point gas model. We provide convincing numerical evidence that the figure of merit ZT diverges as a power law with the average particle number in the chain. This quite surprising result appears to be related to the ergodic and mixing properties of the system and it is independent of the mass ratio.

Keywords: transport processes/heat transfer (theory), dynamical processes (theory)

J. Stat. Mech. (2009) L03004

Understanding the dynamical origins of macroscopic behavior of non-equilibrium systems is one of the major and long standing challenges of statistical mechanics. The main issue is not only related to the understanding of fundamental aspects, but also has important practical implications. For example, the possibility of converting waste heat into useful work, or conversely, of performing refrigeration via thermoelectric phenomena is becoming one of the main challenges for the not far distant future in order to meet the increasing world demand for energy. In spite of the fact that the basic principles of thermoelectric engines have been well known for a long time, the practical suitability is greatly limited by the low efficiency of all known thermoelectric materials [1]–[3].

Indeed the efficiency of a thermoelectric material for energy conversion or electronic refrigeration is given by the non-dimensional thermoelectric *figure of merit*

$$ZT = \frac{\sigma S^2 T}{\kappa}, \tag{1}$$

where σ is the electric conductivity, S is the Seebeck coefficient, κ is the thermal conductivity and T is the absolute temperature. For a given material, and a pair of temperatures $T_{\rm H}$ and $T_{\rm C}$ of hot and cold baths respectively, ZT is related to the efficiency η of converting heat to work, under optimized conditions, through

$$\eta = \frac{P}{J_Q} = \eta_{\rm carnot} \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}, \tag{2}$$

where $\eta_{\rm carnot} = 1 - T_{\rm C}/T_{\rm H}$ is the Carnot efficiency, $T = (T_{\rm H} + T_{\rm C})/2$, P is the output power and J_Q is the heat current. For the best known thermoelectric materials the figure of merit at room temperatures is below the value $ZT = 3$ which is the estimated threshold for thermoelectric devices to become competitive with compressor based refrigeration, for example.

In a recent letter [10] an interesting mechanism has been discovered for increasing ZT in a classical dynamical system. The model, based on classical ergodic dynamics, is an idealized polyatomic gas with $d_{\rm int}$ internal degrees of freedoms. Here the figure of merit has been found to be a growing function of the number of internal degrees of freedom $ZT = (d + 1 + d_{\rm int})/2$ where d is the geometric dimension.

In spite of the abstract nature of the model, the above letter opens the possibility for a theoretical understanding of the basic microscopic requirements that a classical dynamical system must fulfil in order to lead to a high figure of merit and therefore to thermoelectric efficiency which, in principle, is arbitrarily close to Carnot's.

In this letter we make a first step in this direction. Here we consider the thermoelectric efficiency in a hard-point interacting one-dimensional gas. Indeed, a heuristic hint taken from [10] might suggest that inter-particle interaction increases the effective number of degrees of freedom and thus leads to a higher figure of merit than in the non-interacting idealized d-dimensional gas, where $ZT = (d + 1)/2$ [9, 10].

This is quite a speculative hypothesis which should be confirmed by an accurate numerical analysis. In the following we undertake a detailed numerical study of the cross heat and particle transport [4, 5], in an open hard-point gas, and evaluate ZT. As a result we find, very interestingly, that ZT diverges as a power law in the thermodynamic limit, $ZT \propto N^b$ where N is the average number of particles in the system and $b \approx 0.79$.

We recall that, due to the equivalence between electric and chemical potentials [6], it is sufficient to study non-equilibrium effects due to the chemical potential difference only.

Our model is a one-dimensional, di-atomic disordered chain, of hard-point elastic particles with coordinates $x_{\mathrm{i}} \in [0, L]$, velocities v_{i} and masses $m_i \in \{1, M\}$ randomly distributed (we use convenient non-dimensional units). The particles interact among themselves through elastic collisions only. A collision between two particles with mass m_1 and m_2 changes their velocities v_1 and v_2 as $v_1' = [(m_1 - m_2)/(m_1 + m_2)]v_1 + [2m_2/(m_1 + m_2)]v_2$ and $v_2' = [2m_1/(m_1 + m_2)]v_1 - [(m_1 - m_2)/(m_1 + m_2)]v_2$. Two thermochemical baths *inject* and *absorb* particles at the two ends of the system $x_{\mathrm{L}} = 0$, $x_{\mathrm{R}} = L$. We notice that thermal properties of a similar model, with periodically arranged masses $1, M, 1, M, \ldots$, have been previously extensively studied [11]–[13]. It has been found that even though the model appears to be ergodic and dynamically mixing for generic mass ratio M, the decay of temporal correlation functions seems too slow for the validity of diffusive transport laws and convergence of Green–Kubo formulae; hence the thermal conductivity was found to diverge as $\kappa \propto N^{\nu}$, with $\nu \approx 0.3$. As a consequence, in order to have divergence of the figure of merit ZT in the thermodynamical limit, we must count on an even faster increase with N of σ or S.

A thermochemical bath generates particles with randomly chosen mass 1 or M (with equal probability), at some fixed rate γ. Since injections from a macroscopic bath should be independent events, the time interval t between subsequent injections is taken to satisfy the exponential distribution $P(t) = \gamma \mathrm{e}^{-\gamma t}$, where $t_0 = 1/\gamma$ is the average time between injections. Note that the injection rate γ_λ is simply related to the temperature T_λ, and the chemical potential μ_λ, of either of the baths $\lambda = \mathrm{L}, \mathrm{R}$, through

$$\mu_\lambda = T_\lambda \log\left(\frac{c_0 \gamma_\lambda}{T_\lambda}\right). \tag{3}$$

The arbitrary scaling constant c_0 is set to 1 throughout the letter. The injected particles have the velocity distribution $P(v_i) = (m_i/T_\lambda)|v_i|\mathrm{e}^{-(m_i v_i^2)/(2T_\lambda)}$, which ensures the canonical (Maxwellian) distributions under the equilibrium conditions $T_{\mathrm{L}} = T_{\mathrm{R}}$ and $\mu_{\mathrm{L}} = \mu_{\mathrm{R}}$. Note that in our units, $k_{\mathrm{Boltzmann}} = 1$.

Any gas particle which hits the bath, at $x = 0, L$, is absorbed by the bath, so the steady state is reached where the density of particles ρ obeys the thermodynamic equation of state $\rho T = \mathrm{const}$. For convenience we introduce the two independent heat bath parameters $\alpha_\lambda \equiv \mu_\lambda / T_\lambda$ and $\beta_\lambda \equiv 1/T_\lambda$. We note that in the equilibrium situation the particle density satisfies the relation

$$\rho(\alpha, \beta) = c(M)\beta^{-1/2}\mathrm{e}^{\alpha}, \tag{4}$$

where $c(M)$ is some constant which can depend only on the mass ratio M.

Note that a more sophisticated model of thermochemical reservoirs, where each species of particles would have a different injection rates and chemical potentials, essentially gives results equivalent to those reported below [14].

In order to calculate the temperature/particle density profiles we divide our sample $x \in [0, L]$ into a set of small boxes (intervals). Suppose that during a long period of simulation time, a box with length l is visited N_{v} times, where the jth visit is by a particle with mass $m_j^{(\mathrm{v})}$ and velocity $v_j^{(\mathrm{v})}$, and the visit lasts for a time interval t_j. Then, the particle density ρ, the temperature T and the energy density $\frac{1}{2}\rho T$ are calculated as $\rho \equiv (tl)^{-1}\sum_{j=1}^{N_{\mathrm{v}}} t_j$, $T \equiv (\sum_{j=1}^{N_{\mathrm{v}}} m_j^{(\mathrm{v})}[v_j^{(\mathrm{v})}]^2 t_j)/(\sum_{j=1}^{N_{\mathrm{v}}} t_j)$, $\frac{1}{2}\rho T \equiv (tl)^{-1}\sum_{j=1}^{N_{\mathrm{v}}} \frac{1}{2} m_j^{(\mathrm{v})}[v_j^{(\mathrm{v})}]^2 t_j$. Simulating the gas under the non-equilibrium conditions we found that a linear profile of

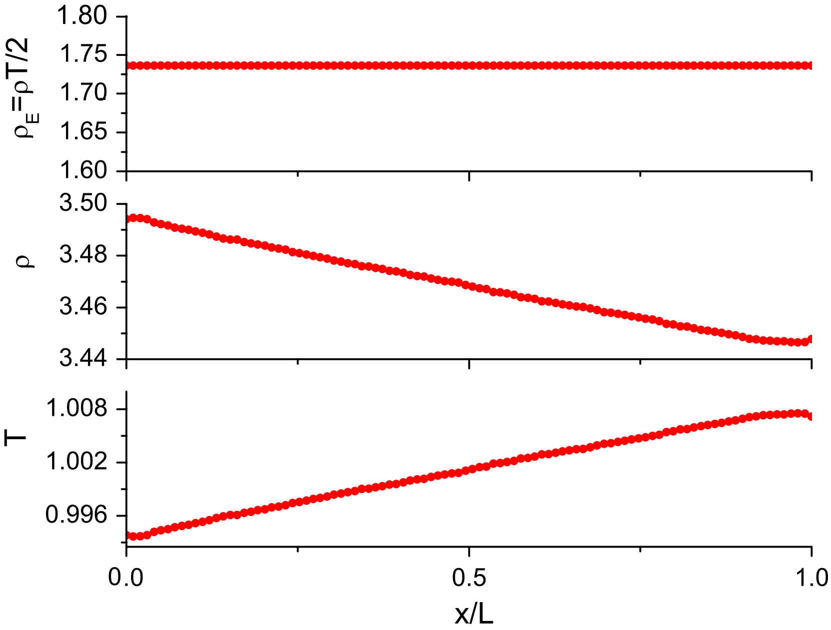

Figure 1. Energy density, particle density, and temperature profiles in a disordered hard-point gas inside two thermochemical baths with fixed $\alpha_{\mathrm{L}} = \alpha_{\mathrm{R}} = \alpha_0$, here putting mean $\alpha_0 = 0$, but slightly different β around $\beta_0 = 1$. Namely $\beta_{\mathrm{L,R}}$ is determined by equation (4) with $\rho_{\mathrm{L,R}} = \rho(\alpha_0, \beta_0)(1 \pm D_\rho)$, where $D_\rho = 0.01$. Notice that the energy density is constant across the system.

temperature $T(x)$ and density $\rho(x)$ is built up (shown in figure 1), whereas the energy density is—as expected—constant across the system.

Note that an isolated one-dimensional hard-point gas has three *conservation laws*: of the total energy, the number of particles, and the total momentum (due to translational invariance), so the corresponding currents should satisfy the continuity equations. In the steady state these are given, respectively, by the injection minus the absorption rates of the particle's energy, the particle's number count and the particle's momentum, at the left bath or, with the opposite signs, at the right bath.

Suppose that in a period of time t, the *left* heat bath injects N_{i} particles with masses $m_j^{(\mathrm{i})}$, and velocities $v_j^{(\mathrm{i})}$, $j = 1, \ldots, N_{\mathrm{i}}$, and absorbs N_{a} particles with masses $m_j^{(\mathrm{a})}$, and velocities $v_j^{(\mathrm{a})}$, $j = 1, \ldots, N_{\mathrm{a}}$. Notice that for the left bath $v_j^{(\mathrm{i})}$ is always positive, and $v_j^{(\mathrm{a})}$ is always negative, while for the right bath the signs would be just the opposite. In the large t limit, the energy current J_u, the particle current J_ρ and the momentum current J_m, are computed as follows:

$$J_u = \frac{1}{2t}\left(\sum_{j=1}^{N_{\mathrm{i}}} m_j^{(\mathrm{i})}[v_j^{(\mathrm{i})}]^2 - \sum_{j=1}^{N_{\mathrm{a}}} m_j^{(\mathrm{a})}[v_j^{(\mathrm{a})}]^2\right), \tag{5}$$

$$J_\rho = \frac{1}{t}(N_{\mathrm{i}} - N_{\mathrm{a}}), \tag{6}$$

J. Stat. Mech. (2009) L03004

$$J_m = \frac{1}{t}\left(\sum_{j=1}^{N_{\rm i}} m_j^{\rm (i)} v_j^{\rm (i)} - \sum_{j=1}^{N_{\rm a}} m_j^{\rm (a)} v_j^{\rm (a)}\right). \tag{7}$$

In the steady state they should be equal to the corresponding currents for the right bath—with the signs changed. For numerical simulations it turns out that the statistical error is reduced if one takes the average of the contributions from the two baths.

Let us now write the phenomenological non-equilibrium thermodynamic relations for our model. By means of the 2×2 Onsager matrix $L_{\tau,\omega}$, $\{\tau, \omega\} \in \{u, \rho\}$, the energy and the particle currents can be written in terms of gradients of thermodynamic potentials $\alpha = \mu/T$ and $\beta = 1/T$ as follows [7, 8]

$$J_u = L_{uu}\nabla\beta - L_{u\rho}\nabla\alpha, \tag{8}$$

$$J_\rho = L_{\rho u}\nabla\beta - L_{\rho\rho}\nabla\alpha. \tag{9}$$

Expressing the Onsager matrix in terms of the phenomenological transport coefficients S, κ and σ one arrives at the very simple expression for the figure of merit

$$ZT = \frac{L_{u\rho}^2}{\det L}. \tag{10}$$

Note that the additional mean chemical potential term (see e.g. [9]) can be set to zero for the ideal gas systems. Note also that a higher value of ZT is obtained when the matrix L tends to being singular, i.e. when the two currents become nearly proportional to each other as functions of $\nabla\alpha$ and $\nabla\beta$.

Let us first discuss the somewhat trivial case of equal masses $M = 1$ in which the gas particles are essentially non-interacting so that the energy and particle currents can be expressed analytically as

$$J_u = T_{\rm L}\gamma_{\rm L} - T_{\rm R}\gamma_{\rm R}, \qquad J_\rho = \gamma_{\rm L} - \gamma_{\rm R}. \tag{11}$$

Using the expression of the chemical potential (3), the Onsager coefficients can be analytically calculated: $L_{uu} = 2{\rm e}^\alpha\beta^{-3}L$, $L_{\rho u} = {\rm e}^\alpha\beta^{-2}L$, $L_{u\rho} = {\rm e}^\alpha\beta^{-2}L$, $L_{\rho\rho} = {\rm e}^\alpha\beta^{-1}L$, thus leading to $ZT = 1$. These values of Onsager coefficients were also confirmed by numerical simulation.

We consider now the non-trivial, non-equal mass case, $M \neq 1$. First, as expected, we have found that the figure of merit ZT, which is a dimensionless quantity, depends only on the average number of particles N, and on the mass ratio M. In figure 2 we display the dependence $ZT(N)$ for a given mass ratio $M = \pi$. For small average particle number, a particle injected by one bath will be, quite probably, absorbed by the other bath without colliding with another particle; thus we expect to recover the result for the non-interacting gas. This means that $ZT(N \to 0) = 1$. By increasing the particle number N we find a highly non-trivial behavior, namely a power law divergence of ZT. The overall behavior can be globally well captured by a phenomenological relation:

$$ZT - 1 = aN^b, \qquad a = 0.255, b = 0.785. \tag{12}$$

As is clear also from figure 2, results are very sensitive to non-linear response effects. Indeed the Onsager coefficients and the numerical estimate for ZT converge to a constant value only for very small gradients of the thermodynamic fields, which can be characterized

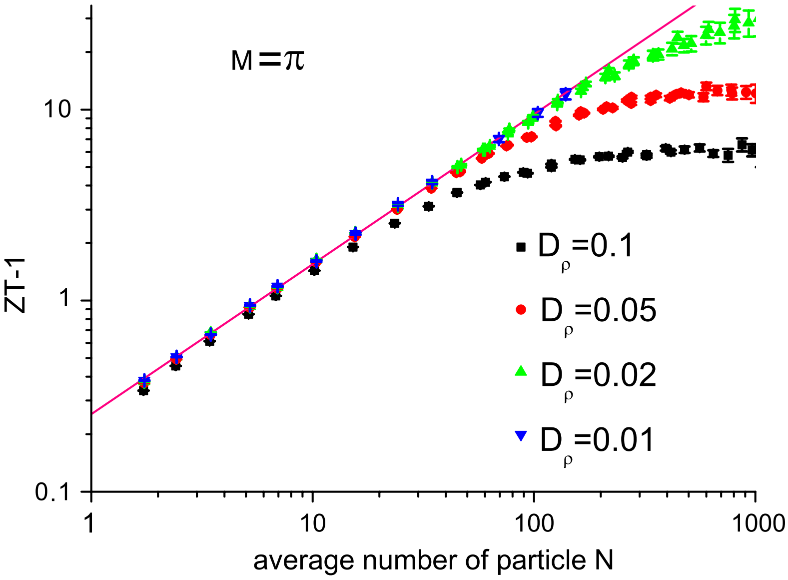

Figure 2. The figure of merit ZT as a function of average number of particles N on a log–log scale, for $M = \pi$. Different symbols refer to different values of the relative density gradient D_ρ (see the legend), whereas the full line corresponds to the power law fit (12). Note that for fixed D_ρ, different values of the mean inverse temperature β, mean α and size L have been considered (namely, we (i) put $L = 100, \beta = 1.0$ and varied α, (ii) put $L = 100, \alpha = 0$ and varied β, and (iii) put $\alpha = 0, \beta = 1.0$ and varied L), but the resulting ZT clearly depends on the average number of particles N *only*. Note also the convergence of numerical results to the asymptotic power law (12) as $D_\rho \to 0$.

by the *relative density gradient* D_ρ, which is defined by boundary (bath) values of the density $\rho_{\mathrm{L,R}}$, as $D_\rho = (\rho_{\mathrm{R}} - \rho_{\mathrm{L}})/(\rho_{\mathrm{R}} + \rho_{\mathrm{L}})$. In figure 3 we show in more detail the non-linear effect of the finite relative density gradient D_ρ, by plotting ZT versus D_ρ for different N. Again we observe clear convergence as $D_\rho \to 0$. In the region of $N < 140$, ZT saturates when D_ρ is about 0.02 or less.

Nevertheless, in the linear regime $D_\rho \to 0$ we find a divergence $ZT \to \infty$ in the thermodynamic limit $N \to \infty$. This is the main result of this letter.

In order to calculate the Onsager coefficients for a given value of α and β, say for $\alpha = 0$, $\beta = 1$, we follow the same procedure as in [10]. We first calculate L_{uu} and $L_{\rho u}$ by setting $\alpha_{\mathrm{L}} = \alpha_{\mathrm{R}} = 0$, and specifying a certain small relative density gradient D_ρ we obtain the inverse temperatures $\beta_{\mathrm{L,R}}$ using the relation (4). Then, we calculate $L_{u\rho}$ and $L_{\rho\rho}$ by setting $\beta_{\mathrm{L}} = \beta_{\mathrm{R}} = 1$ and, again, $\alpha_{\mathrm{L,R}}$ are determined by equation (4) for a given small D_ρ.

Finally we consider the dependence of ZT on the mass ratio M. In figure 4 we display ZT versus M for a fixed average particle number, i.e., for each M we fix N by adjusting the mean value of $\alpha = \mu/T$, which directly affects the mean density (4). Note a cusp-like minimum at $M = 1$, corresponding to the integrable case, where $ZT = 1$. This minimum becomes sharper and sharper when N increases, so we expect that in the thermodynamic limit the value $M = 1$ will become an isolated (integrable) point, whereas for any other

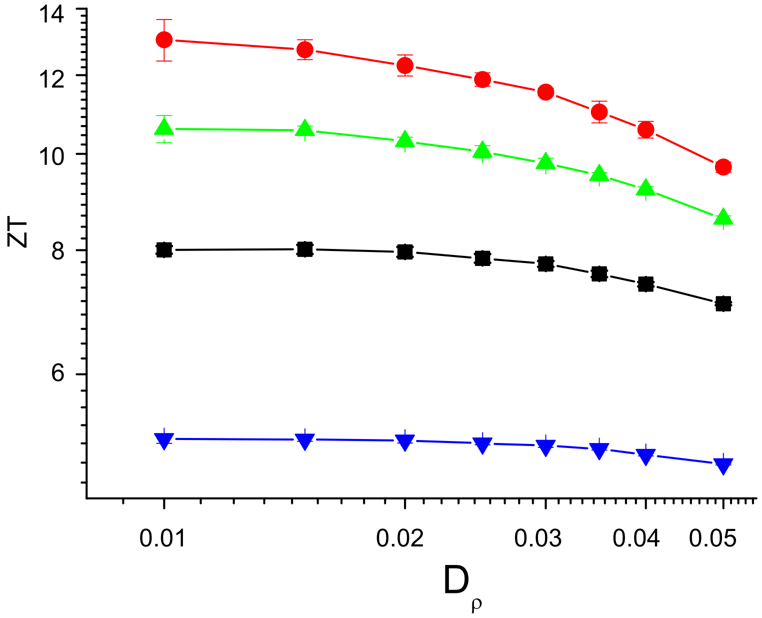

Figure 3. The figure of merit ZT as a function of the relative density gradient D_ρ for several different values of the length of the lattice $L = 10, 20, 30, 40$, which correspond to an average particle number $N = 35, 70, 104, 140$, for curves from below to above. Note that convergence takes place for smaller and smaller D_ρ as the average particle number N increases.

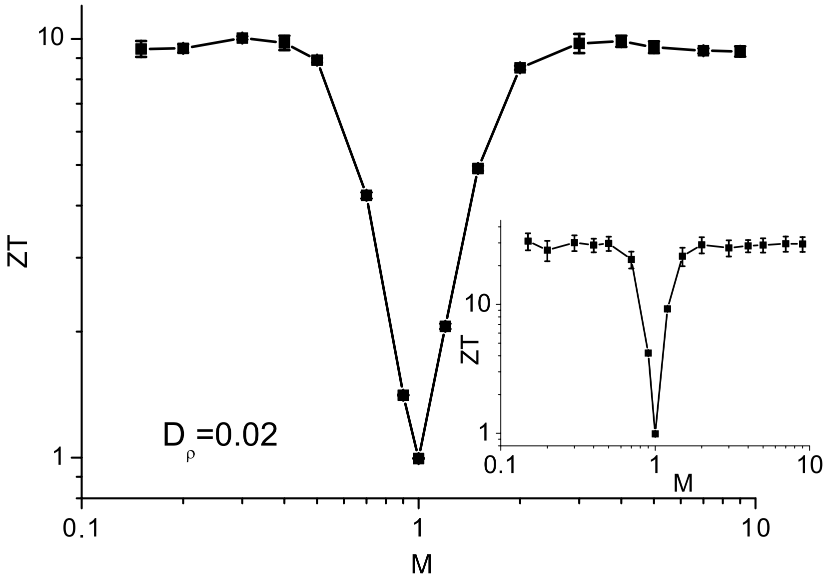

Figure 4. ZT as a function of M for fixed $N = 100$. Inset: ZT as a function of M for fixed $N = 1000$. Note that in the latter case, $D_\rho = 0.02$ is not small enough and the asymptotic value of ZT is not yet reached. Computations with smaller D_ρ, at such large value of N, are beyond the reach of our computers (see figure 3).

J. Stat. Mech. (2009) L03004

$M \neq 1$, corresponding to ergodic and mixing dynamics, ZT is expected to grow with N with the same power law (12).

Perhaps, one might note that the validity of non-equilibrium thermodynamics and the linear response relations (9) should be questioned in detail for systems with anomalous thermodynamic ($N \to \infty$) scaling of transport coefficients. For this purpose we have measured the efficiency (the ratio P/J_Q in equation (2)) via direct numerical experiment. This has been done by inserting a potential barrier against the direction of the particle's current so that one can extract useful work. The height of the barrier which particles needed to climb was optimized in order to yield the highest efficiency, and this number was found to be in perfect agreement with the right-hand side of (2) where ZT is computed via the Onsager matrix elements (e.g. equation (10)).

In conclusion, we have demonstrated that in a very simple, interacting many-particle classical dynamical system, namely the hard-point gas of unequal mass particles in one dimension, the figure of merit ZT diverges to infinity in the thermodynamic limit with a power law in the number of particles which is reminiscent of the divergence of thermal conductivity found earlier in the studies of the Fourier law [11]–[13].

The next obvious step is to implement the hard-point gas system in a working operative model of a heat engine or refrigerator which performs in a steady cycle.

The work is supported by the National Natural Science Foundation of China Grant No. 10874243 and the start-up grant of Renmin University of China (LW).

References

[1] Mahan G, Sales B and Sharp J, 1997 *Phys. Today* **50** 42
[2] Majumdar A, 2004 *Science* **303** 777
[3] Dresselhaus M S *et al*, 2007 *Adv. Mater.* **19** 1043
[4] Maes C and van Wieren M H, 2005 *J. Phys. A: Math. Gen.* **38** 1005
Vollmer J, Tell T and Mátyás L, 2000 *J. Stat. Phys.* **101** 79
Van den Broeck C, 2007 *Advances in Chemical Physics* vol 135, ed S A Rice (New York: Wiley)
[5] Mejia-Monasterio C, Larralde H and Leyvraz F, 2001 *Phys. Rev. Lett.* **86** 5417
[6] Walstrom P L, 1988 *Am. J. Phys.* **56** 890
See also Larralde H, Leyvraz F and Mejia-Monasterio C, 2003 *J. Stat. Phys.* **113** 197
[7] Domenicali C A, 1954 *Rev. Mod. Phys.* **26** 237
[8] Callen H B, 1948 *Phys. Rev.* **73** 1349
de Groot S R and Mazur P, 1984 *Non-Equilibrium Thermodynamics* (New York: Dover)
[9] Vining C B, 1997 *Mater. Res. Soc. Symp. Proc.* **478** 3
[10] Casati G, Mejia-Monasterio C and Prosen T, 2008 *Phys. Rev. Lett.* **101** 016601
[11] Dhar A, 2001 *Phys. Rev. Lett.* **86** 3554
[12] Grassberger P, Nadler W and Yang L, 2002 *Phys. Rev. Lett.* **89** 180601
[13] Casati G and Prosen T, 2003 *Phys. Rev.* E **67** 015203(R)
[14] Wang J, 2008 private communication