Entropy Measurement in Strongly Coupled Complex Plasmas

Frank Wieben* and Dietmar Block
IEAP, Christian-Albrechts-Universität, D-24098 Kiel, Germany

(Received 19 June 2019; revised manuscript received 9 October 2019; published 26 November 2019)

The change in entropy of a system that is transferred between two states at different temperatures is measured in a two-dimensional plasma crystal experiment. One- and especially two-component dust clusters are confined in the plasma sheath and heated to different temperatures using laser manipulation. We find that entropies obtained from the phase space yield consistent results for, i.e., the heat capacity which shows excellent agreement with the Dulong-Petit law. The implications for the validity of basic thermodynamical principles in finite size complex (dusty) plasmas are discussed.

DOI: 10.1103/PhysRevLett.123.225001

Thermodynamics looks back at a long and successful history in physics, although there are still open questions or even disputes related to the very fundamentals [1,2]. In statistical mechanics the systems' thermodynamic properties can be extracted from the phase space, e.g., through the state function entropy. Many-body systems that allow us to directly measure the phase space information of all particles are rare. Besides colloidal dispersions [3,4], complex (dusty) plasmas provide full access to the phase space on the single particle level [5]. Because of high negative particle charges of several thousand elementary charges and moderate kinetic temperatures the particles in a complex plasma form strongly coupled layers in fluid or crystalline states. Such plasma crystals are a unique model system for one-component plasmas (OCP), like-charged particles embedded in a uniform background of neutralizing charges [6,7]. In theory, OCPs are fully characterized with respect to thermodynamic properties using the coupling parameter Γ and screening strength κ [8,9]. Several experiments including phase transitions [10,11], diffusion [12,13], and fluctuation theorems [14] show that complex plasmas are adequately described by OCP theory. In this light, it is tempting to take an even closer look at the very fundamental thermodynamics of complex plasmas. There are three essential questions that arise here and which we aim to answer in this Letter. Despite certain nonequilibrium processes and instabilities [15] in complex plasmas, do the basic thermodynamic principles hold? How important is the system size, i.e., are small systems with a few particles sufficient to apply thermodynamics? Does the screened interaction in complex plasmas favor the equivalence of microcanonical and canonical ensembles as theory predicts for short-range interacting systems [16]?

In this Letter, we propose an experiment that serves as a benchmark for the thermodynamics of small plasma crystals. In order to maintain the OCP description a method which solely varies a single parameter is required. Temperature has been proven to be this particular parameter. In complex plasma research, laser heating is a well-established technique to increase the kinetic temperature of plasma crystals [17], without affecting other properties of the discharge or the particles, e.g., their charge [18]. If the temperature of a thermodynamic system changes due to the transfer of heat from or to the system the total entropy changes accordingly. The change in entropy ΔS of a system undergoing a reversible process from state A to state B is

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T} = C \ln\left(\frac{T_B}{T_A}\right), \qquad (1)$$

where $dQ = CdT$ is the transfer of heat from or to the system and C is its heat capacity. Thus, for a system where both the temperatures and heat capacity are known ΔS is directly determined. Since entropy is a state function, the analysis of the system in the equilibrium states A and B yields ΔS regardless of the exact transition process. An irreversible process can be transformed into a reversible one by introducing additional auxiliary thermal reservoirs to take the system quasistatically, at any moment in thermal equilibrium, from state A to state B. Equation (1) describes a single system undergoing a temperature change, e.g., a cooling process but can be expanded to systems composed of any number of subsystems. While monodisperse systems would represent the most simple case (see Supplemental Material [19]), we choose to share our experiments with binary mixtures in this Letter. As we will demonstrate, we are able to create a situation where two particle species reside in the same volume but attain different temperatures. The temperature ratio can be controlled externally [20].

A schematic of the thermodynamic transition in our experiments is shown in Fig. 1. Consider two systems 1 and 2 initially (state A) at different temperatures or each in contact with a thermal reservoir with T_1 and T_2. In the second and final state both systems are in thermal

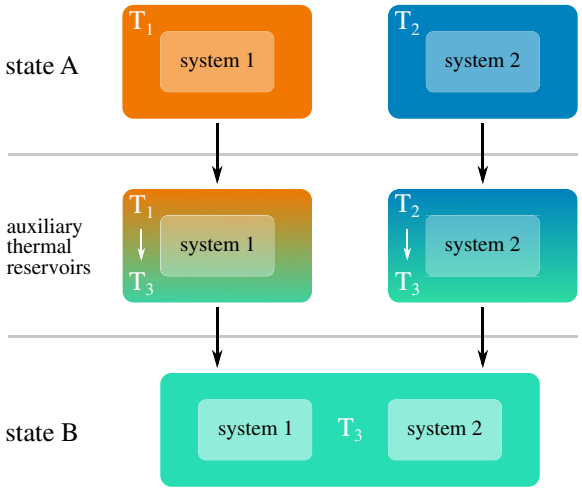

FIG. 1. Schematic of the thermodynamic transition process. State A: Two systems are initially at different temperatures T_1 and T_2. State B: The systems are brought into thermal contact with a third thermal reservoir at $T_3 = T_B$. To make this process reversible, auxiliary thermal reservoirs are introduced.

equilibrium with a third thermal reservoir at $T_3 = T_B$. Utilizing additivity, the change in entropy of both systems is

$$\Delta S = C_1 \ln\left(\frac{T_3}{T_1}\right) + C_2 \ln\left(\frac{T_3}{T_2}\right). \tag{2}$$

In our case T_3 is given by the neutral gas background. To fulfill Eq. (2) for given $C_{1,2}$ the total change in entropy must match the temperature changes of the subsystems.

Our experimental scenario is a binary mixture complex plasma [21–23], a system composed of two particle species with different sizes. After injection into the plasma, the dust particles charge due to collection of electrons and ions to negative charges of $q_d \approx 10^3 e$ and subsequently become trapped in the sheath of a radio frequency discharge. The micron sized particles form a two-dimensional layer and interact via a screened Coulomb potential [24]. Low damping ensures minimal dissipation of energy and allows us to observe dynamical processes. Particles are illuminated with a red laser sheet and imaged using standard video microscopy. Positions and velocities of all particles are extracted from the camera images. The two different systems are realized using spherical melamine-formaldehyde (MF) and silica (SiO_2) particles, where the MF and SiO_2 particles will form systems 1 and 2, respectively. By choosing particle sizes $a_{1,2}$ and mass densities $\rho_{1,2}$ to fulfill the condition $a_1/a_2 = \sqrt{\rho_2/\rho_1}$ two-dimensional binary systems are prepared (see Ref. [22] for details). Energy is put into the systems using a laser heating setup [17], that utilizes the force a laser beam exerts on the particles. In our case four opposing laser beams with a well-balanced momentum input ($\langle \mathbf{p} = 0 \rangle$) are scanned stochastically across the particle cluster, applying random kicks. In this way, the kinetic temperature of the system is increased. Such setups have proven to isotropically heat particle clusters and yield Maxwell-Boltzmann velocity distributions. Thus, laser heating serves as a thermal reservoir. To realize the different temperatures of the species or systems a disparity in the laser-particle interaction is utilized. The magnitude of the laser force, and thus the kinetic temperature, depends on the very specific particle properties (size, refractive index). Monodisperse particle ensembles take a uniform temperature distribution. This is not the case for binary mixtures, consisting of particles of different sizes and materials. Because of photophoresis [25], the MF particles attain higher kinetic temperatures in our experiment [20].

Ergodicity as well as the equipartition theorem are assumed to hold for this classical system. Then, the heat capacity of our system with N charged particles that interact via a repulsive potential is the Dulong-Petit law $C = 2fk_B/2 = 2Nk_B$, where f is the number of degrees of freedom. Since both kinetic and potential energy contribute to the heat capacity, an additional factor of 2 is introduced. We rewrite Eq. (2) to adapt it to our two-component system and insert the Dulong-Petit law. This yields

$$2k_B = \frac{\Delta S}{N_{\mathrm{MF}} \ln(\frac{T_3}{T_{\mathrm{MF}}}) + N_{\mathrm{SiO_2}} \ln(\frac{T_3}{T_{\mathrm{SiO_2}}})}. \tag{3}$$

The aim of this Letter is to check this equality for small plasma crystals (monodisperse and binary), thus serving as a benchmark experiment. For this, some preconditions have to be exactly met. The laser heating is tuned to produce Maxwell-Boltzmann velocity distributions, the laser-particle interaction intrinsically yields a two temperature system and the lhs of Eq. (3) is the control parameter we use to verify the correct thermodynamic behavior of our system. All quantities on the rhs of Eq. (3) are directly determined from the positions and velocities of the particles in the experiment. No additional fitting parameter is introduced. The kinetic temperatures are obtained from the velocity distributions, i.e.,

$$T_{\mathrm{kin}} = \frac{m}{k_B} \langle \sigma^2_{v_{x,y}} \rangle, \tag{4}$$

where σ_v is the standard deviation of the distributions and m is the particle mass specified by the manufacturer.

To follow a more fundamental approach we use the microcanonical instead of the canonical description. How to exactly determine the entropy from the phase space is still heavily debated [1,2]. While this is an interesting question for future experiments, it does not affect our measurements. In the thermodynamic limit or for a sufficient amount of degrees of freedom, volume and surface entropies become equivalent [26] since for a highly dimensional phase space the volume is mostly concentrated in its

outer shell. For the sake of computational simplicity we use the volume of the phase space to determine the entropy. The volume entropy of a microcanonical ensemble reads

$$S(E) = k_B \ln \Omega_{E'<E}, \tag{5}$$

where the partition function $\Omega_{E'<E}$ is the number of microstates within the $2f$-dimensional phase space volume V up to energy E. Since for this experiment only the change in entropy is of interest, the problem reduces to finding the ratio of phase space volumes. The investigated systems are two dimensional and of a circular shape on the one hand and particle motion is well described by Maxwell-Boltzmann velocity distributions on the other hand. Thus, the general shape of phase space is preserved and its $4N$-dimensional volume can be approximated with a $4N$-dimensional bounding box (cuboid). This volume differs from the *true* volume only by a geometrical factor that cancels out when the change in entropy $\Delta S = k_B \ln (V_B/V_A)$ is calculated. Numerically, ΔS is then obtained from a sampled phase space using

$$\frac{\Delta S}{k_B} = \sum_{n=1}^{2N} [\ln (\delta q_{n,B} \delta p_{n,B}) - \ln (\delta q_{n,A} \delta p_{n,A})]. \tag{6}$$

Here, q and p are generalized coordinates and momenta, respectively, and δ marks the maximum extent of $q \in \{x_1 ... x_N, y_1 ... y_N\}$and $p \in \{p_{x,1} ... p_{x,N}, p_{y,1} ... p_{y,N}\}$ in each dimension. This completes the set of quantities necessary to check the equality in Eq. (3), which again are all readily obtained from the experiment.

Laser heating is applied to small binary clusters with particle numbers ranging from $N = 100$ to 200 particles. MF admixture to SiO_2 particles is in the range of 40%–60%. Trajectories of a binary cluster with 100 particles are shown in Figs. 2(a) and 2(b) in the heated and unheated state. Particle species are distinguished via light scattering. Without the additional thermal reservoir of the laser heating the particles perform thermal motion closely around their equilibrium positions due to collisions with the background gas. Corresponding velocity distributions are plotted in (c) and (d) and compared to Gaussian fits. Since the cluster attains equilibrium states in A and B, ergodicity is assumed and distributions are computed from time series of 500 frames for all particles of each species. In general, the velocity distributions of the species differ to a greater extent when heated. From the standard deviations the kinetic temperatures are obtained using Eq. (4). A typical temperature evolution before and after switching off the laser is shown in Fig. 3. In (a) the kinetic temperature of each species is plotted individually. While the cluster is heated the kinetic temperatures differ by a factor of $T_{\mathrm{MF}}/T_{\mathrm{SiO_2}} \approx 2.2$. Once the lasers are turned off, both species relax into a state where their temperatures almost match ($|\Delta T_{\mathrm{kin}}| \approx 20$ K). This can be seen from the absolute

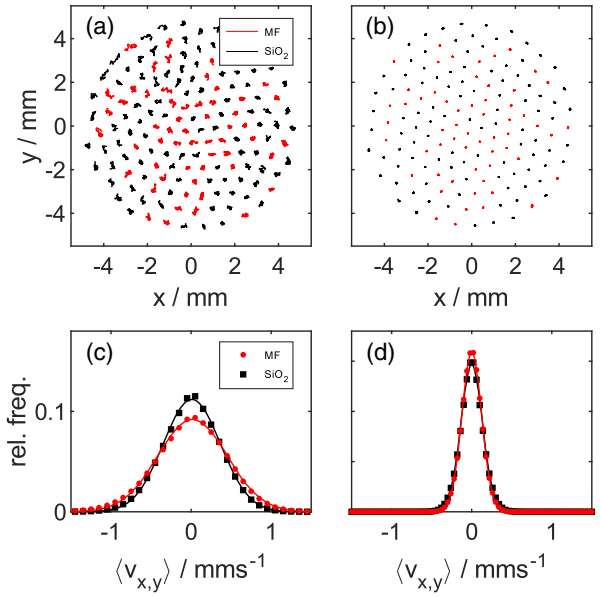

FIG. 2. Trajectories and corresponding velocity distributions of a binary particle cluster with $N = 100$ particles in the heated (a), (c) and relaxed state (b),(d). Trajectories are shown for a single measurement and 200 consecutive frames. Velocity distributions are computed from 500 frames and averaged over the x and y directions with approximately 50 measurements.

temperature difference plotted in (b). Because of switching off the thermal reservoir of the laser heating T_3 is smaller than both T_1 and T_2 and thus the entropy of systems 1 and 2 decreases from state A to state B. The temperature levels of

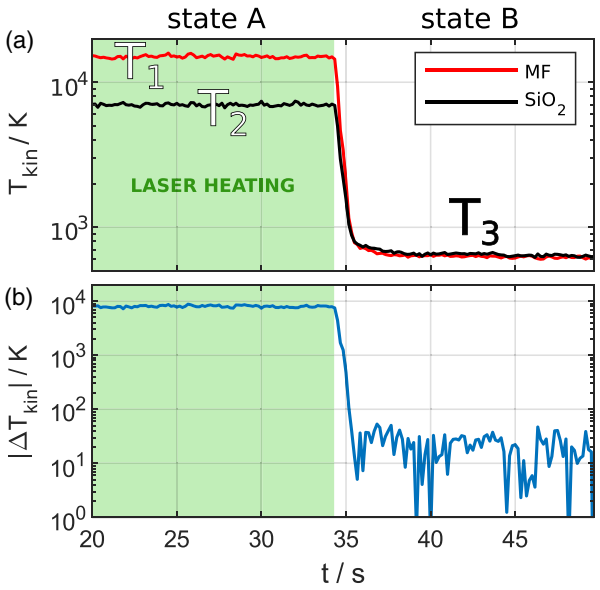

FIG. 3. Kinetic temperatures of each particle species (a) and absolute difference in kinetic temperature (b). While the laser is switched on (green shaded) the system is in state A. As soon as the laser is turned off, the particles quickly relax into state B, where the temperatures almost match.

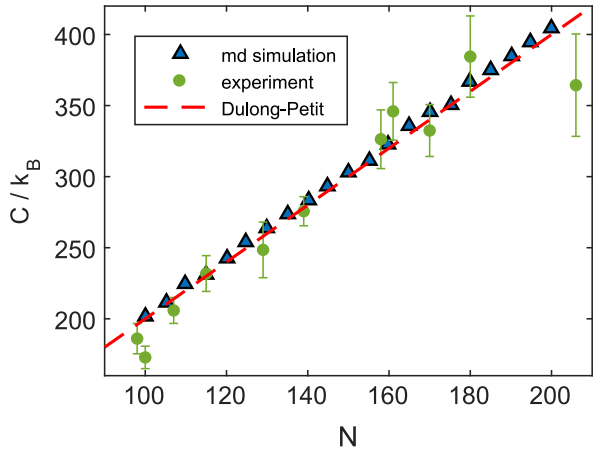

FIG. 4. Right-hand side of Eq. (3) compared to the Dulong-Petit heat capacity $C = 2k_B N$ obtained from experiments and numerical simulation with different particle numbers N.

MF and SiO_2 before and after switching off the laser are now identified as the temperatures T_1, T_2, and T_3 from Eq. (2). Note that T_3 does not depend on the temperatures $T_{1,2}$ but originates from the coupling to the thermal reservoir of the neutral gas background. Experimental data as well as simulation results of the rhs of Eq. (3) are shown as a function of particle number in Fig. 4. Additional molecular dynamics simulations with two particle species and parameters chosen as close as possible to the experiment have been carried out. A modified Langevin-thermostat is used to reproduce the different temperature levels. The overall agreement of both simulation and experiment is staggering. Simulation and measurement show maximum deviations from the Dulong-Petit law of about $\Delta C_{\mathrm{sim}} < 1\%$ and $\Delta C_{\mathrm{meas}} < 15\%$, respectively. This agreement is achieved with particle samples that exhibit Gaussian statistics and in parameter regimes where no instabilities emerge (see Supplemental Material [19]). Although the velocity distributions show slight deviations from pure Gaussian distributions which could hint at nonequilibrium effects, this could very well be attributed to too short time series [27]. To investigate this in detail, a robust analysis of non-Gaussianity has been employed [28]. Within the margins of error the deviation from Gaussian statistics is negligible. Note that no fitting process is involved, as all parameters are determined from the experiment. Comparable results are achieved using monodisperse systems (see Supplemental Material [19]). Thus, we can state that small two-dimensional plasma crystals (monodisperse and binary) of approximately 10^2 particles obey the very fundamental thermodynamics and represent a unique model system with full phase space access.

These findings have interesting consequences. The particles reside in the thermal reservoirs provided either by the neutral gas background or the laser heating thermostat and thus would require a canonical treatment. Nonetheless, the microcanonical description using the phase space to compute the entropy yields very good agreement with Dulong-Petit without any additional parameters. This is a fundamental result and the first experiment directly confirming the equivalence of ensembles in strongly coupled complex plasmas. This is expected from the theory for short-range interactions [16] and matches the exponential character of a screened Coulomb interaction very well.

For comparison, Dulong-Petit heat capacities have also been found in other two-dimensional systems, e.g., paramagnetic particles with dipole-dipole interactions [29] and related Yukawa systems [30]. While this Letter does not answer the question how to exactly obtain the entropy from the phase space (volume or surface entropy), very consistent results are achieved using the volume. Complex plasmas thus are a good candidate to contribute to this question in the future with more refined experiments.

Remarkable about the scenario in our experiment is the fact that two particle species reside in the same volume but take different temperatures. In this way the change in configurational entropy during this process is minimized. In particular, the experimental apparatus is not limited to produce only Maxwell-Boltzmann velocity distributions. The laser heating algorithm controlling the scanning mirrors can be tuned to produce, e.g., Tsallis distributions [31]. This makes laser heated two-dimensional complex plasmas an ideal model system to study the detailed influence of the underlying statistics on thermodynamics in the future.

This work has been funded by the DFG (Deutsche Forschungsgemeinschaft) under Research Grant No. BL555/3-1.

*wieben@physik.uni-kiel.de

[1] J. Dunkel and S. Hilbert, Nat. Phys. **10**, 67 (2014).
[2] R. H. Swendsen and J.-S. Wang, Phys. Rev. E **92**, 020103(R) (2015).
[3] H. Boroudjerdi, Y.-W. Kim, A. Naji, R. Netz, X. Schlagberger, and A. Serr, Phys. Rep. **416**, 129 (2005).
[4] S. R. Nagel, Rev. Mod. Phys. **89**, 025002 (2017).
[5] G. E. Morfill and A. V. Ivlev, Rev. Mod. Phys. **81**, 1353 (2009).
[6] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).
[7] M. Bonitz, C. Henning, and D. Block, Rep. Prog. Phys. **73**, 066501 (2010).
[8] O. S. Vaulina and S. A. Khrapak, J. Exp. Theor. Phys. **90**, 287 (2000).
[9] P. Hartmann, G. J. Kalman, Z. Donkó, and K. Kutasi, Phys. Rev. E **72**, 026409 (2005).
[10] V. A. Schweigert, I. V. Schweigert, A. Melzer, A. Homann, and A. Piel, Phys. Rev. Lett. **80**, 5345 (1998).
[11] A. Melzer, A. Schella, J. Schablinski, D. Block, and A. Piel, Phys. Rev. Lett. **108**, 225001 (2012).
[12] S. Nunomura, D. Samsonov, S. Zhdanov, and G. Morfill, Phys. Rev. Lett. **96**, 015003 (2006).

[13] B. Liu and J. Goree, Phys. Rev. Lett. **100**, 055003 (2008).
[14] C.-S. Wong, J. Goree, Z. Haralson, and B. Liu, Nat. Phys. **14**, 21 (2018).
[15] A. Melzer, Phys. Rev. E **90**, 053103 (2014).
[16] H. Touchette, Europhys. Lett. **96**, 50010 (2011).
[17] J. Schablinski, D. Block, A. Piel, A. Melzer, H. Thomsen, H. Kählert, and M. Bonitz, Phys. Plasmas **19**, 013705 (2012).
[18] F. Wieben, J. Schablinski, and D. Block, Phys. Plasmas **26**, 033701 (2019).
[19] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.225001 for complementary results of monodisperse systems and a discussion of nonequilibrium effects.
[20] F. Wieben and D. Block, Phys. Plasmas **25**, 123705 (2018).
[21] C. Killer, T. Bockwoldt, S. Schütt, M. Himpel, A. Melzer, and A. Piel, Phys. Rev. Lett. **116**, 115002 (2016).
[22] F. Wieben, J. Schablinski, and D. Block, Phys. Plasmas **24**, 033707 (2017).
[23] D. Block and A. Melzer, J. Phys. B **52**, 063001 (2019).
[24] U. Konopka, G. E. Morfill, and L. Ratke, Phys. Rev. Lett. **84**, 891 (2000).
[25] S. Beresnev, V. Chernyak, and G. Fomyagin, Phys. Fluids A **5**, 2043 (1993).
[26] P. Buonsante, R. Franzosi, and A. Smerzi, Ann. Phys. (Amsterdam) **375**, 414 (2016).
[27] E. Milotti, Phys. Rev. E **83**, 042103 (2011).
[28] E. de Santa Helena, C. Nascimento, and G. Gerhardt, Physica (Amsterdam) **435A**, 44 (2015).
[29] S. Deutschländer, A. M. Puertas, G. Maret, and P. Keim, Phys. Rev. Lett. **113**, 127801 (2014).
[30] O. S. Vaulina, I. E. Drangevski, X. G. Adamovich, O. F. Petrov, and V. E. Fortov, Phys. Rev. Lett. **97**, 195001 (2006).
[31] C. Tsallis, Eur. Phys. J. Spec. Top. **226**, 1433 (2017).