Non-equilibrium systems are ubiquitous in nature.

Equilibrium systems are ideal and can only be achieved in laboratory. Attempts have been made to understand the dynamics of non-equilibrium systems by linear response theory [1] albeit their domains of validity are restricted to the linear response regime. There exists no general formalism to deal with systems that are far from equilibrium. For a system out of equilibrium, the probability of a given microstate evolves continuously with time. In the long time limit the system reaches a stationary state in which the probability measure over the configuration space converges to a constant distribution. Non-equilibrium systems display fluctuations which are less sensitive to the conditions of the surroundings and carry information about the dynamics of their present state. In the last decade certain general relations have been discovered which are valid for non-equilibrium systems and are independent of how far the system is driven out of equilibrium. These results include the Jarzynski equality [2,3] and the fluctuation theorems [4–12]. They have been verified for a variety of systems theoretically as well as experimentally [13–17].

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After the work by Crooks [7] and Seifert [8], it is now understood that many of these relations are closely related to the probability density function (PDF), $p(x,t)$, of the corresponding diffusion process. Here $x$ denotes the variable collecting the fluctuations and is referred to as the diffusion variable. The scaling property of $p(x,t)$ is evaluated by means of the sub-trajectories $x_n(t) = \sum_{i=0}^{n} \xi_{i+n}$ with $n = 0, 1, \ldots, \text{etc.}$. If the scaling condition $p(x,t) = t^{-\delta} F(x t^{-\delta})$ holds true, it is easy to prove that the entropy $S(t)$ is given
by \( S(t) = -\int_{-\infty}^{\infty} p(x, t) \ln[p(x, t)]dx = A + \delta \ln(t) \), where \( A \) is a constant. This indicates that in the case of a diffusion process with a scaling PDF, its entropy \( S(t) \) increases linearly with \( \ln(t) \). One can also examine the scaling properties of the second moment of the same process by FVSM. One version of FVSM is the Standard Deviation Analysis (SDA) [19], which is based on the evaluation of the standard deviation \( D(t) \) of the variable \( x \), and yields \( D(t) = [(x^2; t) - \langle x; t \rangle^2]^\frac{1}{2} \propto t^H \) [19]. The exponent \( H \) is interpreted as the scaling exponent. For random noise with finite variance, the diffusion distribution \( p(x, t) \) will converge, according to the central limit theorem, to a Gaussian distribution with \( H = \delta = 0.5 \). If \( H \neq \delta \), the scaling represents anomalous behavior. Levy walk is a kind of anomalous diffusion which is obtained by generalizing the central limit theorem [20]. In this particular kind of diffusion process the scaling exponents \( H \) and \( \delta \) are found to obey the relation \( \delta = (3 - 2H)^{-\frac{1}{2}} \) instead of being equal [19].

To generate the non-equilibrium model system we have utilized the MD simulation technique in an innovative way. Depending on the interaction potential model, a typical MD simulation computes the trajectories of atoms in a system by solving Newton’s equations of motion numerically. In our study, the simulations have been performed for elements having different crystal structures like silicon (Si) and germanium (Ge) with a diamond cubic structure, iron (Fe) and molybdenum (Mo) with body-centered cubic structure and copper (Cu), aluminium (Al) and solid argon (Ar) having face-centered cubic structure. Thus, a variety of interaction potential models have been employed (see table 1) in the simulations. For all these elements, periodic boundary conditions are imposed along three directions \((x, y, z)\) in the simulation cell. Initially, all the systems are equilibrated using constant energy and volume ensemble (NVE) at 100 K for 2.5 ps except for Ar, where the equilibration run is performed at 30 K for 10 ps. The kinetic energy in the equilibrium state will follow a Boltzmann distribution. The period of time for equilibration is chosen to be sufficient to bring the total energy of the system to divide approximately equally between kinetic energy (KE) and potential energy (PE). Details of the parameters used in the simulations like simulation cell size, number of atoms taken in the simulation cell, the time steps after which simulation data are recorded and the nature of the inter-atomic potentials used for the elements under study are given in table 1. To generate the non-equilibrium state, the three components of velocities of an individual atom in the simulation cell were changed to random values such that the instantaneous KE of the atom increases, however the average temperature of the system corresponds to \( T = 500 \) K (\( T = 70 \) K for Ar). The atoms in the simulation cell are then allowed to equilibrate. After a sufficiently long period of time, the system is observed to attain an equilibrium temperature of 300 K (50 K for Ar) and the average kinetic energy becomes equal to the average potential energy of the respective systems. The variations of temperature (equivalent to KE) with time of the systems of Ar and Cu leading to equilibration are shown in fig. 1. Atomistic simulation data are recorded for each time step for the entire equilibration time to study the dynamic nature of the equilibration process. The MD simulations are carried out using the MD++ simulation package [21].

Few atoms in the simulation cell are identified in a sphere of radius “\( r \)” whose centre is chosen to be almost at the middle of the cell, far away from the surface. The values of “\( r \)” and the number of atoms in the sphere for

| Material | Si | Ge | Cu | Solid Ar | Mo | Fe | Al |
|----------|----|----|----|----------|----|----|----|
| Simulation cell size (in unit cell) | 25\(^3\) | 15\(^3\) | 20\(^3\) | 20\(^3\) | 25\(^3\) | 25\(^3\) | 20\(^3\) |
| Number of atoms in simulation cell | 125000 | 27000 | 32000 | 32000 | 31250 | 31250 | 32000 |
| Simulation time step (fs) | 0.25 | 0.5 | 0.5 | 2.0 | 0.5 | 0.5 | 0.5 |
| Nature of inter-atomic potential used | SW | SW | EAM | LJ | FS | FS | GLUE |
| Total number of data taken | 6000 | 3000 | 3000 | 10000 | 3000 | 3000 | 3000 |
| Radius “\( r \)” (Å) | 8.8250 | 9.0809 | 5.4766 | 7.9952 | 6.2944 | 5.7330 | 6.1566 |
| No. of atoms in the sphere of radius “\( r \)” | 150 | 147 | 55 | 55 | 63 | 63 | 55 |
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Fig. 1: (Colour on-line) Variations of temperature (equivalent to KE) with time of the systems of (a) Ar and (b) Cu leading to equilibration.

Each simulation are given in table 1. The KE in the consecutive time steps for the atoms in the sphere is used for further analysis. In these simulations the atoms in the simulation cell are kept isolated from the environment and hence there was no dissipation of energy, only there is a redistribution of KE and PE among the atoms. DEA and SDA analyses [22] were performed for the time series data of the KE for an individual atom. Typical plots of DEA and SDA analysis from which $\delta$ and $H$ are calculated for a Copper atom are shown in fig. 2. The slopes of the curves evaluate $\delta$ and $H$. DEA and SDA analyses were performed for ten atoms randomly chosen from the atoms confined in the sphere of radius "$r$" and the average of the values of $\delta$ and $H$ are given in table 2. The simulation cell sizes, the number of atoms in the cell, the sampling time, the crystal structure, and the nature of the interaction potential were varied to find the exact nature of the scaling.

To understand the process of equilibration when a single excited atom interacts with an ensemble of atoms that are in equilibrium, another kind of exercise was performed by MD simulation. In this case from the equilibrated ensembles of Si, Cu, Fe at 300 K and solid Ar at 50 K one atom in the middle of the cell was excited to a KE corresponding to 500 K and 70 K, respectively. The excited atom is then allowed to equilibrate and the KE possessed by the atom at different time steps was monitored. In these simulations the energy of the simulation cells was also a constant of motion. All the equilibrated atoms in the cell form a heat bath and the excited atom equilibrates by interacting with this heat bath by sharing its excess KE. The time series thus obtained of the KE of the excited atom between consecutive time steps was used to understand the diffusion process of KE and the nature of the dynamical process responsible to bring the atom to the equilibrium state. The values of $\delta$ and $H$ obtained by DEA and SDA from the time series are given in table 2.

Atoms in the simulation cell, when brought to a non-equilibrium state by enhancing their KE, try to redistribute their excess KE by the process of diffusion. This process of redistribution of KE among the atoms changes their mean positions of vibration and consequently their PE. Here all the atoms in the cell participate together in the diffusion process. Thus by analyzing the variation of the KE with time for a single atom in the cell one can account for the modality of this diffusion process and the nature of the equilibration. The change in the KE for an atom in the $i$-th time step is given by $\Delta E = (2E_{m})^{1/2} F_i \Delta t$, where $F_i$ is force on the atom at the $i$-th time step. The force field experienced by an atom in the cell will consist of three parts. The deterministic force, arising from the nearest-neighbor interaction potential, plays the role of the external force $F(t)$ acting on the atom. There will be an energy exchange between the atom and the surrounding atoms as a result of which the atom loses a part of its KE for exciting various degrees of freedom of the atoms in the ensemble; moreover, there will be an increase in the PE in the cost of the atom KE. This can be described with help of a frictional force $F_f(t)$ acting on the atom. Besides losing KE due to a frictional effect there is the possibility of gaining KE in the form of a random movement of the atom due to interactions from all other atoms in the cell and which can be modeled by a random force $\Gamma(t)$ acting on the atom. $\Gamma(t)$ will have the property $\langle \Gamma(t) \rangle = 0$ and $\langle \Gamma(t_1)\Gamma(t_2) \rangle = Ag(\Delta t)$, where $\Delta t = (t_2 - t_1)$, the function $g(t)$ dies down rapidly with $t$ and $A$ is the strength of the random force and is a function of temperature $T$. Thus,
Table 2: Mean values of the scaling exponents $\delta$ and $H$ obtained from ten atoms chosen randomly in the shell of radius “r”. Exponents $\delta$ and $H$ are evaluated from the time series of the evolution of KE for a single atom.

| Material         | Non-equilibrium temperature (K) | $\delta$          | $H$          | $\left(\frac{\delta - \frac{1}{3}}{\frac{1}{2\pi}}\right) \times 100$ |
|------------------|---------------------------------|-------------------|--------------|-------------------------------------------------------------------|
| Si               | 500                             | 0.953 ± 0.016     | 0.968 ± 0.008| 1.380                                                             |
| Si               | 800                             | 0.898 ± 0.025     | 0.901 ± 0.025| 7.046                                                             |
| Si (single atom) | 500                             | 0.943             | 0.970        | 0.042                                                             |
| Ge               | 500                             | 0.930 ± 0.021     | 0.953 ± 0.026| 1.712                                                             |
| Ge               | 800                             | 0.930 ± 0.020     | 0.960 ± 0.015| 0.438                                                             |
| Ar               | 70                              | 0.968 ± 0.010     | 0.968 ± 0.005| 2.908                                                             |
| Ar (single atom) | 70                              | 0.963             | 0.972        | 1.665                                                             |
| Cu               | 500                             | 0.920 ± 0.020     | 0.955 ± 0.022| 0.279                                                             |
| Cu (single atom) | 500                             | 0.935             | 0.978        | 2.444                                                             |
| Fe               | 500                             | 0.925 ± 0.018     | 0.964 ± 0.022| 0.847                                                             |
| Fe (single atom) | 500                             | 0.959             | 0.974        | 0.879                                                             |
| Mo               | 500                             | 0.935 ± 0.016     | 0.964 ± 0.021| 0.231                                                             |
| Al               | 500                             | 0.935 ± 0.008     | 0.966 ± 0.013| 0.142                                                             |

the dynamics of the atoms will follow a Langevin-type equation [23]. To see the effect of this random force field on the scaling behavior, the ensembles of Si and Ge atoms were exited to a higher temperature, i.e. at 800 K and were allowed to equilibrate at 450 K. The $\delta$ and $H$ values for the time series of the KE for these cases are given in table 2. As the systems were allowed to equilibrate on their own without any defined protocol, forces acting on the atoms are time dependent through the dynamical process of equilibration. The force field experienced by an atom in the simulation cell in the $i$-th time step is calculated from its velocities, at $(i-1)$-th, $i$-th, $(i+1)$-th time steps. Typical mean values of these forces are $1.011654 \times 10^{-10} \text{N}$ and $24.7088 \times 10^{-10} \text{N}$ for solid argon and Si, respectively. The fluctuating part of the force field at different time steps was obtained by subtracting the mean values. Typical probability distributions for the fluctuating part of the force field in the case of solid Ar and Si atoms are shown in fig. 3. The distributions are Gaussian with center $-6.69 \times 10^{-12} \text{N}$ and width $9.59 \times 10^{-11} \text{N}$ for Ar and the corresponding values for Si are $-4.98 \times 10^{-11} \text{N}$ and $1.95 \times 10^{-10} \text{N}$, respectively. To understand the correlation of the fluctuating force field, vectors $\{|X_i\rangle\}$ are generated from the time series data of the fluctuating force field by taking consecutive $n$ time steps for constructing each vector. The eigenvalue spectra of the covariance matrix $\Sigma_x$ of these vectors are calculated to establish the nature of the correlation. Figure 4 shows typical eigenvalue spectra for Ar and Si cases. The flatness of the spectra confirms that the fluctuating force fields are uncorrelated.

The motion of the atoms in the simulation cell is thus governed by these forces and dictates the variation of KE of the atoms. The memory effect of the initial velocity will die down with time. In the long time limit the system equilibrates leading to equipartition of energy. The characteristic of the variation of KE in terms of time series indicates the evolution of the non-equilibrium state. To understand the universality of this evolution for different dynamical processes as generated by MD simulations, the Shannon entropy of the diffusion process of KE of an
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The exact inherent dynamics of the process of transmitting excess KE of an atom to its surroundings could not be revealed from this analysis. However, this analysis reflected the underlying generic features and physical principles that are independent of the detailed dynamics or characteristics of a particular model. The diffusion of the KE of an atom to its surroundings is a continuous stationary stochastic process as the probability of the diffusion trajectories follows a scaling relation. As the exponent $H$ is greater than 0.5 for all cases, the diffusion is an anomalous superdiffusion. Any diffusion is a kind of random walk and the Levy walk is a mathematical model to describe anomalous superdiffusion where the scaling exponent of variance against time is greater than one. Levy walks have coupled space-time probability distributions and are characterized by a cluster of smaller variations of the random variable with a few large variations between them. This pattern repeats for all scales. As the process of equilibration of the KE of an atom in the ensemble from its non-equilibrium state has to be very rapid, it cannot be of Brownian type and it should be of Levy-walk type as Levy walk will outperform Brownian walk during the process of equilibration. The Levy-walk type of diffusion of KE among the atoms may be due to the following reason. Excess KE of an atom should be distributed locally; however, there is a finite probability to transport its excess KE to a distant atom and consequently this atom again redistributes its KE in the same process. This process is much faster than normal diffusion when the mean squared value of fluctuation depends on $t$ only. Mostly three-dimensional systems show normal diffusion except in glassy systems [24]. The anomalous or superdiffusion and Levy walks have been observed in various real-life phenomena like fluid flow in rotating annulus [25], low-dimensional heat transport [26], light scattering in porous media [27] etc. However, our findings show that the diffusion of KE for a single atom in its non-equilibrium state, when embedded in an environment of atoms that are either in equilibrium or in non-equilibrium state, show superdiffusion and Levy-walk properties throughout the process of equilibration. In the case when a single atom interacts with the ensemble of atoms that are in equilibrium we can assume that the atom is interacting with a thermal bath by absorbing or releasing KE without appreciable change in the bath state. In this case also we see that the diffusion of KE from the atom is a Levy-walk process.

Atoms of crystals, when brought to a non-equilibrium state, try to redistribute their energy amongst them to converge to an equilibrium distribution. This fundamental process is governed by the increase in entropy of the trajectories of the individual atom and should be identical in nature for all types of elemental atoms and will be independent of the nature of interactions between the atoms and the perturbation which brought them to a non-equilibrium state. The calculation of the Shannon entropy of the diffusion process was made for one atom. However, the concept of entropy in statistical mechanics is for an
ensemble. But the entropy production for a single trajectory has been addressed in the literature [8] concerning fluctuation theorems.

Atoms in a lattice possessing a KE different from its equilibrium values at any instant of time try to transport or accept KE from the nearest neighbors and arrive at a new value. The time series of this KE were translated into a diffusion process in the form of diffusion trajectories and PDFs of these trajectories were estimated. The estimated Shannon entropy production of this dynamical process with time is found to obey a universal scaling relation. This scaling relation is exact and valid for systems no matter how far they are driven out of equilibrium and is independent of the strength of perturbation that brought the system out of equilibrium.

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