

Inhomogeneity of Local Temperature in Small Clusters in Microcanonical Equilibrium

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(Received 2 August 2006; published 6 July 2007)

Overall homogeneity of temperature is a condition for thermal equilibrium, but, as is demonstrated by classical molecular dynamics simulations, the local temperatures of atoms in small, isolated crystalline clusters in microcanonical equilibrium are not uniform. The effective temperature determined from individual atomic velocity decreases with distance from the cluster center. It is argued that these effects are due to the conservation of angular and translational momentum. A general microcanonical expression is derived for the spatial dependence of the statistics of the kinetic energies of individual atoms; this fits the numerical observations well.

DOI: [10.1103/PhysRevLett.99.014102](https://doi.org/10.1103/PhysRevLett.99.014102)

PACS numbers: 36.40.Sx, 36.40.Qv

Introduction.—Small systems such as microclusters consisting typically of 10 – 10^3 atoms and molecules are regarded as a new phase of matter which is intermediate between microscopic and macroscopic objects. The direct outcome of the smallness of the system has been found in exotic stable structures, the lowering melting temperature [1], anomalous structural fluctuation of Au clusters [2,3], negative heat capacity [4], rapid alloying of binary metal clusters [5,6], the coexisting state of liquid and solid phase [7], and so forth. Molecular dynamics (MD) simulation and Monte Carlo (MC) simulation have been powerful tools to analyze these phenomena peculiar to microclusters. Indeed several groups have performed classical microcanonical MD simulations which provide microscopic insight into the dynamical behavior of small clusters [8]. In such studies, the *kinetic temperature* is defined as the averaged kinetic energy per a individual spatial degree of freedom (DOF), and has played a significant role in establishing a relationship between thermodynamic quantities and MD data. One might, ideally prefer to use the *thermodynamic temperature*, defined by reciprocal of the derivative of the Boltzmann entropy with respect to the energy, supposing that the MD simulation generates data which are compatible with a microcanonical ensemble.

Because the evaluation of Boltzmann entropy is not so easy for a given Hamiltonian system one compromises to employ *kinetic temperature* instead of *thermodynamic temperature*. Even if a given system satisfies ergodic condition, however, there still exists an ambiguity in the definition of temperature. Since in usual experimental conditions, in addition to the total energy, there are conserved quantities such like total translational and angular momenta which affect the microcanonical measure in a non-trivial manner [9]. In fact, in molecular beam experiments on unimolecular reactions, both total energy and angular momentum are predetermined and assumed to be conserved. In those cases, because of the conserved quantities, the resultant velocity distribution of each atom is expected to be altered especially in a system with the small number of DOF. If a microcluster with sufficiently large number of

atoms has no conserved quantities other than the total energy, the velocity distribution computed by time average or ensemble average over constituent atoms will closely follow a Maxwell-Boltzmann (MB) distribution under ergodic condition and the values of the *local* temperature characterizing the velocity distribution of *each single atom* should be the same at microcanonical equilibrium. However, in the presence of additional conserved quantities, the obtained values of the *local* temperature do not necessarily imply the same value for each atom. Thus the spatial uniformity of the temperature would not be satisfied any more even at a microcanonical equilibrium, as demonstrated below.

The purpose of this Letter is to elucidate numerically and theoretically the reason why the conservation of total angular and translational momentum results in nonuniformity of *local* temperature characterizing the velocity distribution of individual atoms and in the appearance of apparent temperature gradient in microclusters containing a small number of atoms, although the system is in the microcanonical equilibrium.

Numerical results.—First we provide numerical evidence that the *local* kinetic temperature is *nonuniform* over small, microcrystalline clusters; see Fig. 1(a). The results are obtained by a microcanonical MD simulation. Since the inhomogeneity of the kinetic temperature is particularly enhanced in binary clusters with notably different masses as mentioned later, we exemplify two cases implied by MD results for the alkali-halide clusters $(\text{NaI})_{13}\text{I}^-$ and $(\text{NaI})_{32}$, each of which has a rock-salt structure. The average total kinetic energy is taken to be small enough so that the cluster is in the solid phase. We depict in Fig. 1(a) the frequency distribution of kinetic energy κ for Na^+ on the surface of the cluster and that for I^- at the center of the cluster. While these two curves are both fitted very well by the MB distribution, they provide the different values of the local temperatures T_{eff} , which are determined by the MB distribution $P(\kappa) \propto \sqrt{\kappa} e^{-\kappa/k_B T_{\text{eff}}}$. In addition, we numerically confirm that the local temperature of the MB distribution agrees quite well with the local kinetic

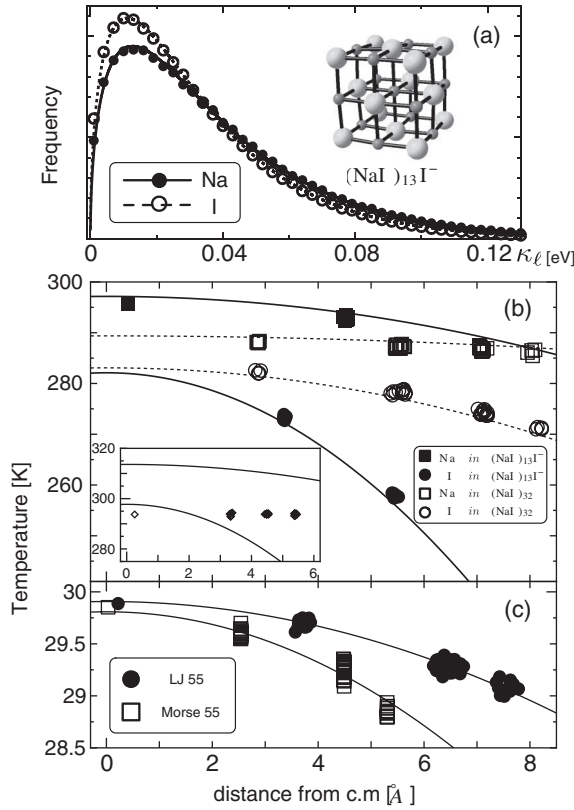


FIG. 1. (a) The frequency distributions of the kinetic energy of the Na atom (solid circle) at center and the I atom (white circle) at surface and the corresponding MB distribution for $(\text{NaI})_{13}\text{I}^-$. There is a distinct difference between two shapes of the MB distribution: The values of the local temperature obtained by the fitting are 319 and 278 K, for the Na atom and the I atom, respectively. (b) Dependence of time-averaged kinetic temperature upon the distance of an atom from the center of clusters $(\text{NaI})_{13}\text{I}^-$ and $(\text{NaI})_{32}$ is shown. For the MD simulation, the long-range Tosi-Fumi potential [13] has been adapted. Solid and dotted curves are the theoretical prediction of Eq. (5), for $(\text{NaI})_{13}\text{I}^-$ and $(\text{NaI})_{32}$, respectively. Note that Eq. (5) can be rewritten as $\langle \kappa_\ell \rangle \cong 3[1 - \frac{m_\ell}{M} - \frac{2}{3} \frac{\langle R^2 \rangle}{I} \frac{k_B T(E)}{2}]$; all clusters examined here satisfying the relation $I = I_X \cong I_Y \cong I_Z$. The cold surface and hot core atom spontaneously become apparent for both clusters. The effect of the conservation of the angular momentum is clearly demonstrated in comparison with the inset, where $(\text{NaI})_{13}\text{I}^-$ is put in the additional asymmetric harmonic potential function, $U(x, y, z) = \epsilon_{xx}x^2 + \epsilon_{yy}y^2 + \epsilon_{zz}z^2$, where $(\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}) = (5.0, 10, 7.0)[10^{-3} \text{ eV}/\text{\AA}^2]$, respectively. By the long time MD simulation over $1 \mu\text{s}$ it turns out that the values of averaged kinetic energies are almost the same, and that the energy equipartition is attained for every Na and I atom. (c) Kinetic temperatures for icosahedral clusters of 55 atoms of equal mass interacting via the short-range Morse and Lennard-Jones (6–12) potentials. One can verify the validity of the theoretical prediction.

temperature determined by the time-averaged kinetic energy of the individual atom. Thus we term both temperatures as local temperature hereafter. In Fig. 1(b) we show how the local temperature of individual atoms depends on

the distance of the atom from the center of the cluster. It is evident that the local temperatures of atoms of the same species decreases systematically as the distance from the center increases. The local temperature gradient is enhanced as the number of atoms decreases. In the $(\text{NaI})_{13}\text{I}^-$ cluster, the local temperature on the surface is 15% lower than the local temperature at the center.

This phenomenon would be similarly observed in any kind of small clusters irrespective of the nature of the forces binding the atoms. Indeed, as shown in Fig. 1(c), data of icosahedral Morse and Lennard-Jones (LJ) clusters composed of 55 atoms show an evident position dependence of local temperature. For numerical validity, all the MD data are taken over a sufficiently long period over 100 nsec in order to confirm that the statistical error (typically less than a few percent) is much less than the difference among the local kinetic energies. All the MD simulations are done under the condition where we do not observe the evaporation of any atoms. As the small cluster is isolated and the system has the rotational and the translational invariance, the total angular and translational momentum are conserved. To explore the effect of the additional conserved quantities, we put the cluster into a trap described by the asymmetric harmonic potential breaking the rotational and translational symmetry of the system. Then the inhomogeneity of kinetic energy of an individual atom disappears if the asymmetry is strong enough, which suggest that the inhomogeneity is due to the additional conserved quantities [Fig. 1(b)]. We are, therefore, lead to the idea that such an anomalous effect can be well described by the microcanonical ensemble taking fully into account of the constraints due to the conserved total angular and translational momentum.

Analysis based upon the microcanonical measure.—To clarify the essential role of the constraints, we suppose that both the total translational and the angular momenta are zero. Generalization to the case of nonzero total translational and angular momenta is straightforward. The microcanonical measure of the system is expressed by $\rho(\mathbf{q}, \mathbf{p}) \propto \delta(H(\mathbf{p}, \mathbf{q}) - E) \delta(L_{\text{tot}}(\mathbf{q}, \mathbf{p})) \delta(\mathbf{p}_{\text{tot}}(\mathbf{p}))$, where $L_{\text{tot}} = \sum_{i=1}^N \mathbf{q}_i \times \mathbf{p}_i$ and $\mathbf{p}_{\text{tot}} = \sum_{i=1}^N \sqrt{m_i} \mathbf{p}_i$ are the total angular and translational momenta, respectively. In the Hamiltonian $H(\mathbf{p}, \mathbf{q}) = \frac{1}{2} \sum_{i=1}^N \mathbf{p}_i^2 + V(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$ the canonical coordinate pair $(\mathbf{q}_i, \mathbf{p}_i)$ of the i th atom is the mass-weighted coordinate and momentum, which are $(\sqrt{m_i} \tilde{\mathbf{q}}_i, \tilde{\mathbf{p}}_i / \sqrt{m_i})$ (m_i is the mass of the i th atom) in terms of the original coordinate $\tilde{\mathbf{q}}_i$ and momentum $\tilde{\mathbf{p}}_i$, and E is the total energy. The phase space volume of the system is given by $\Omega(E) = \int d\mathbf{q} d\mathbf{p} \theta(E - H(\mathbf{p}, \mathbf{q})) \delta(L_{\text{tot}}(\mathbf{q}, \mathbf{p})) \times \delta(\mathbf{p}_{\text{tot}}(\mathbf{p}))$, which is directly related to entropy, where $\theta(x)$ is the step function [10]. Then the thermodynamic temperature is defined by $T(E) = \Omega(E) / [k_B \Omega'(E)]$. The numerical result shown above, however, indicates that this traditionally defined temperature $T(E)$ no longer specifies the effective temperatures, which represent local temperatures determined by the MB velocity distributions of individual atoms.

We first fix the coordinate variables $\mathbf{q} = {}^t(q_{1x}, q_{1y}, q_{1z}, \dots, q_{Nx}, q_{Ny}, q_{Nz})$ and integrate over $\mathbf{p} = {}^t(p_{1x}, \dots, p_{Nz})$, and finally integrate over \mathbf{q} , where t denotes transpose. Fixing \mathbf{q} , we take the principal axes of the inertia tensor of the cluster as the instantaneous orthogonal frame $O\text{-}XYZ$, along which the momenta and coordinates are measured. Let $\mathbf{Q} = {}^t(Q_{1X}, Q_{1Y}, \dots, Q_{NZ})$ (fixed tentatively) and $\mathbf{P} = {}^t(P_{1X}, P_{1Y}, \dots, P_{NZ})$ be the coordinate and momentum vectors observed in such a frame. We introduce new momenta $\boldsymbol{\xi} = {}^t(\xi_1, \xi_2, \dots, \xi_{3N})$ using the orthogonal matrix \mathbf{T} as $\boldsymbol{\xi} = {}^t\mathbf{TP} = {}^t(\mathbf{e}_1, \mathbf{e}_2, \dots, \mathbf{e}_{3N})\mathbf{P}$. The row vectors $\{\mathbf{e}_i\}$ forming the orthogonal basis, which depends only on \mathbf{q} , are determined in such a way that the first six components represent the three normalized components of the total translational momentum and those of the three normalized components of the total angular momentum, namely, ${}^t(\xi_1, \xi_2, \xi_3) = {}^t(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)\mathbf{P} = {}^t\mathbf{p}_{\text{tot}}/\sqrt{M}$ and ${}^t(\xi_4, \xi_5, \xi_6) = {}^t(\mathbf{e}_4, \mathbf{e}_5, \mathbf{e}_6)\mathbf{P} = {}^t(\frac{L_{\text{tot}X}}{\sqrt{I_X}}, \frac{L_{\text{tot}Y}}{\sqrt{I_Y}}, \frac{L_{\text{tot}Z}}{\sqrt{I_Z}})$. For example, the unit vector \mathbf{e}_4 is given explicitly by $(0, -Q_{1Z}, Q_{1Y}, 0, -Q_{2Z}, Q_{2Y}, \dots, 0, -Q_{NX}, Q_{NY})/\sqrt{I_X}$. The remaining $(3N-6)$ orthogonal unit vectors $\{\mathbf{e}_j\}_{j=7}^{3N}$ are chosen so as to be orthogonal to the six orthonormal vectors. Note that the matrix \mathbf{T} depends on \mathbf{q} and so \mathbf{P} depends on \mathbf{q} and $\boldsymbol{\xi}$, which is explicitly shown by $\mathbf{P} = \mathbf{T}(\mathbf{q})\boldsymbol{\xi}$.

In terms of the new momenta, the total kinetic energy is invariant and is given by $\sum_{i=1}^{3N} \frac{1}{2} \xi_i^2$ because the transformation is orthogonal. Moreover, the constraints for the momentum and for the angular momentum become simply $\xi_i = 0$ for $1 \leq i \leq 6$. Thus the statistical average of any function $X(\mathbf{P}, \mathbf{q})$ of the momenta $\mathbf{P} = \mathbf{T}(\mathbf{q})\boldsymbol{\xi}$ and coordinate \mathbf{q} with respect to the microcanonical measure leads to

$$\langle X(\mathbf{P}, \mathbf{q}) \rangle = \frac{\int d\xi d\mathbf{q} X(\mathbf{T}(\mathbf{q})\boldsymbol{\xi}, \mathbf{q}) \sigma(\boldsymbol{\xi}, \mathbf{q}) / \sqrt{|I(\mathbf{q})|}}{\int d\xi d\mathbf{q} \sigma(\boldsymbol{\xi}, \mathbf{q}) / \sqrt{|I(\mathbf{q})|}}, \quad (1)$$

where $\sigma(\boldsymbol{\xi}, \mathbf{q}) = \prod_{i=1}^6 \delta(\xi_i) \delta(E - \frac{\xi^2}{2} - V(\mathbf{q}))$ is the reduced measure and $|I(\mathbf{q})|$ denotes the determinant of the inertia tensor [11]. Consider the case that the physical quantity $X(\mathbf{P}, \mathbf{q})$, to be averaged, contains only a part of the momentum variables including the first 6 momenta. Let the set of the momenta be ${}^t\xi' = (\xi_1, \dots, \xi_6, \dots, \xi_{6+s})$ ($1 < s < 3N-6$) and $X = X(\xi', \mathbf{q})$, then one can carry out the integration over the remaining momentum variables $\xi_{7+s}, \xi_{8+s}, \dots, \xi_{3N}$ in Eq. (1). The integral is obtained by taking the energy derivative of the phase space volume of $(3N-s-6)$ -dimensional hypersphere, namely, $\sum_{i=s+7}^{3N} \xi_i^2 = 2K(E - \frac{1}{2}\xi'^2, \mathbf{q})$, where $K(E, \mathbf{q}) = E - V(\mathbf{q})$ is the total kinetic energy of the coordinate \mathbf{q} on the energy shell of the total energy E . The result is given by

$$\langle X(\xi', \mathbf{q}) \rangle = C_N \frac{\int d\mathbf{q} d\xi' X(\xi', \mathbf{q}) \hat{\sigma}(\xi', \mathbf{q}) / \sqrt{|I(\mathbf{q})|}}{\int d\mathbf{q} [2K(E, \mathbf{q})]^{(3N-8)/2} / \sqrt{|I(\mathbf{q})|}}, \quad (2)$$

where $\hat{\sigma}(\xi', \mathbf{q}) = \prod_{i=1}^6 \delta(\xi_i) \{2K(E - \frac{\xi'^2}{2}, \mathbf{q})\}^{(3N-8-s)/2}$, $C_N = \frac{(3N-6-s)\pi_{3N-6-s}}{(3N-6)\pi_{3N-6}}$, and π_μ is the volume of

μ -dimensional unit hypersphere. The procedure mentioned above can be also applied straightforwardly to relate the thermodynamic temperature defined before and the ensemble-averaged total kinetic energy $k_B T(E) = \frac{\langle 2K(E, \mathbf{q}) \rangle}{3N-6}$.

Making use of Eq. (2), we can derive a general formula for the moments of kinetic energies partitioned to individual atoms. We describe some details of deriving the expression for the lowest order moment, which can be obtained in a primitive way. That suffices to demonstrate the position dependence of kinetic energy over the cluster. We first construct the remaining orthogonal unit vectors $\{\mathbf{e}_j\}$ ($j \geq 7$) by Gram-Schmidt orthogonalization. Let $\mathbf{a}_{\ell\alpha}$ be the unit vector with the null components except for the $\alpha (= X, Y, Z)$ component of the ℓ th atom. It is used for constructing the new vector as $\mathbf{e}_7 = (\mathbf{a}_{\ell\alpha} - \sum_{j \leq 6} ({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_j) \mathbf{e}_j) / |\mathbf{a}_{\ell\alpha} - \sum_{j \leq 6} ({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_j) \mathbf{e}_j|$, and we get $P_{\ell\alpha} = \sum_{j \leq 7} ({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_j) \xi_j$, because $\{\mathbf{e}_j\}$ for $j \geq 8$ are perpendicular to $\mathbf{a}_{\ell\alpha}$. Noticing that the inner product $({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_j)$ explicitly depends on \mathbf{q} alone, one can compute the mean square average as $\langle P_{\ell\alpha}^2 / 2 \rangle = \langle ({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_7)^2 K(E, \mathbf{q}) \rangle / (3N-6)$ from Eq. (2) by integrating over ξ_7 and by putting $s=1$, where the relation $[2K(E, \mathbf{q})]^{(D+3)/2} = (D+2) \frac{\pi_{D+2}}{\pi_{D+3}} \times \int \xi^2 [2K(E - \xi^2/2, \mathbf{q})]^{D/2} d\xi$ is used. With the contributions from the other components obtained in the same way, the expression for the average of kinetic energy $\kappa_\ell = p_\ell^2/2 = P_\ell^2/2$ of the ℓ th atom becomes

$$\langle \kappa_\ell \rangle = \frac{1}{3N-6} \left\langle \sum_{\alpha=X,Y,Z} e_{\alpha\alpha}^{(\ell)}(\mathbf{q}) K(E, \mathbf{q}) \right\rangle, \quad (3)$$

with the coefficients $e_{\alpha\beta}^{(\ell)} = ({}^t\mathbf{a}_{\ell\alpha} \mathbf{e}_7)({}^t\mathbf{a}_{\ell\beta} \mathbf{e}_7)$ given by

$$e_{\alpha\beta}^{(\ell)} = \delta_{\alpha\beta} \left(1 - \frac{m_\ell}{M} - \frac{Q_{\ell\beta}^2}{I_\gamma} - \frac{Q_{\ell\gamma}^2}{I_\beta} \right) - (1 - \delta_{\alpha\beta}) \frac{Q_{\ell\alpha} Q_{\ell\beta}}{I_\gamma}, \quad (4)$$

where α, β, γ is a cyclic permutation of X, Y, Z , and M is the total mass of the N particles. In particular, if the cluster is in solid phase, deviations of the atoms from their equilibrium positions are much less than the equilibrium interval between nearby atoms and the decoupling approximation $\langle e_{\alpha\alpha}^{(\ell)} K \rangle \cong \langle e_{\alpha\alpha}^{(\ell)} \rangle \langle K \rangle$ would be quite good. The lowest order moment (3) is then given by

$$\langle \kappa_\ell \rangle \cong \left[3 - \frac{3m_\ell}{M} - \sum_{\alpha=X,Y,Z} \frac{\langle R_\ell^2 \rangle - \langle Q_{\ell\alpha} \rangle^2}{\langle I_\alpha \rangle} \right] \frac{k_B T(E)}{2}, \quad (5)$$

where $R_\ell^2 = \sum_\alpha Q_{\ell\alpha}^2$. Equation (5) clearly manifests how the average kinetic energy of the individual atom decreases as the distance of the atom from the center of mass increases. For two different values of mass ratios in Eq. (5), we compare the theoretical curves of Eq. (5) and numerical results, which exhibit excellent agreement for the binary clusters [Fig. 1(b)] and for the single species clusters [Fig. 1(c)]. Remark that $\langle \kappa_\ell \rangle$ loses the position dependence in the limit $N \rightarrow \infty$ because $(\langle R_\ell^2 \rangle - \langle Q_{\ell\alpha} \rangle^2) / I_\alpha$ tends to

zero. The above results allow us to give a simple interpretation to the physical origin of the position dependent mean kinetic energy. Since the translational and rotational motions are collective motions, their energies are, if any, distributed to individual atoms. The second and the third terms in the expanded form of Eq. (5) are, respectively, the translational and the rotational kinetic energies distributed to the ℓ th atom, if the system is in canonical equilibrium at temperature $T(E)$. Thus, a possible interpretation of the origin of the nonuniform individual kinetic energies is that the kinetic energy of an individual atom is reduced by the amount of these two energies provided to the collective motions when the collective motions are at rest. To obtain a general formula for the higher order moments we have to devise a more efficient method of computation. Since the derivation is rather tedious, we only refer to the final result [12]:

$$\langle \kappa_\ell^n \rangle = \sum_{n_1+n_2+n_3=n} \tilde{C}(n_1, n_2, n_3) \langle \nu_1^{n_1} \nu_2^{n_2} \nu_3^{n_3} K(\mathbf{q})^n \rangle, \quad (6)$$

where $K(\mathbf{q}) \equiv K(E, \mathbf{q})$, and $\nu_i = \nu_i^{(\ell)}(\mathbf{q})$ are the roots of the cubic equation

$$\nu(\mathbf{q})^3 + A_\ell(\mathbf{q})\nu(\mathbf{q})^2 + B_\ell(\mathbf{q})\nu(\mathbf{q}) + C_\ell(\mathbf{q}) = 0 \quad (7)$$

with the coefficients $A_\ell(\mathbf{q}) = -\sum_{\alpha=X,Y,Z} e_{\alpha\alpha}^{(\ell)}$, $B_\ell(\mathbf{q}) = \frac{1}{2}\sum_{\alpha\neq\beta} (e_{\alpha\alpha}^{(\ell)}e_{\beta\beta}^{(\ell)} - e_{\alpha\beta}^{(\ell)2})$, $C_\ell(\mathbf{q}) = 2e_{XY}^{(\ell)}e_{YZ}^{(\ell)}e_{ZX}^{(\ell)} - e_{XX}^{(\ell)}e_{YY}^{(\ell)}e_{ZZ}^{(\ell)} + \frac{1}{2}\sum_{\alpha\neq\beta\neq\gamma} e_{\alpha\alpha}^{(\ell)}e_{\beta\gamma}^{(\ell)2}$, and $\tilde{C}(n_1, n_2, n_3) = \prod_{i=1}^3 (n_i - \frac{1}{2})! [(3N-9)\{\frac{1}{2}(3N-11)\}!] / [(3N-6)(\frac{1}{2}(3N-11) + n)!] [\pi_{3N-9}\pi_{3N-8+2n}] / [\pi_{3N-6}\pi_{3N-11+2n}] n! / (n_1!n_2!n_3!)$. In the solid phase the decoupling approximation $\langle \nu_1^{n_1} \nu_2^{n_2} \nu_3^{n_3} K^n \rangle \equiv \langle \nu_1 \rangle^{n_1} \langle \nu_2 \rangle^{n_2} \langle \nu_3 \rangle^{n_3} \langle K^n \rangle$ is available.

The distribution function $P(\kappa)$ can be also obtained by substituting $X = \delta(\kappa_\ell(\mathbf{q}, \xi') - \kappa)$ in Eq. (2) [12]. However, to derive an explicit analytical expression for $P(\kappa)$, we need some approximation. In the present case we use the cumulant expansion for the variable ξ' , and the lowest order approximation leads to the MB distribution $P(\kappa) \propto \sqrt{\kappa} e^{-\kappa/k_B T_\ell}$ with the local effective temperature T_ℓ dependent upon the individual atom, which is given by

$$k_B T_\ell \equiv \frac{2}{(9N-33)} \sum_i \frac{\langle K(\mathbf{q})^{-3/2} / \sqrt{C_\ell(\mathbf{q})} \rangle}{\langle K(\mathbf{q})^{-5/2} / (\nu_i(\mathbf{q}) \sqrt{C_\ell(\mathbf{q})}) \rangle}. \quad (8)$$

If the decoupling approximation is applied, the ratio of $k_B T_\ell$ to the local kinetic energy $\frac{2}{3}\langle \kappa_\ell \rangle$ becomes the common constant which is independent of ℓ and is very close to 1, namely, $\langle K \rangle \langle K^{-5/2} \rangle (3N-11) / [\langle K^{-3/2} \rangle (3N-6)] = 1 - O(\frac{1}{N})$ [9]. Thus, we may claim that the velocity distribution function of the individual atom will closely follow a MB distribution with effective local temperature $\frac{2}{3k_B} \langle \kappa_\ell \rangle$, which is the very fact numerically demonstrated in Fig. 1(a).

Conclusion.—We have shown numerically and theoretically that additional conservation quantities such as the

total angular momentum may result in the inhomogeneity of local temperature in small clusters although the system is in the microcanonical equilibrium. Specifically, the conservation of linear momentum creates a *mass effect* arising from the repartition of the excess $\frac{3k_B T}{2}$ kinetic energy over the individual kinetic DOF while, on the other hand, the conservation of angular momentum results in a systematic decrease of the local temperature with distance from the center of mass yielding a significant temperature gradient. We have derived a basic formula for the moment of kinetic energy of an individual atom and an explicit form of distribution for kinetic energy of individual atoms, both of which agree quite well with numerical results. The present results shows that the local temperature cannot be used as the indicator of microcanonical equilibrium when the number of atoms of the system is large, but is not very large.

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