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van der Waals type loop in microcanonical caloric curves of finite systems

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The entropy is usually related to the energy density of states. This relation is approximate for the finite systems (clusters) and an exact relation connects the entropy with the phase volume of the system. These relations give the same results only in the thermodynamic limit. We consider the microcanonical caloric curves determined via both the approximate and exact relations. It is proved that if the caloric curve obtained from the exact relation has a van der Waals type loop (or S bend), then the caloric curve obtained from the approximate relation has S-bend, and the reverse statement is not correct. Using properties of the system at low and high energies we have shown that a van der Waals type loop in the caloric curve of the finite system requires a positive value of the second derivative of the logarithm of the canonical total energy distribution function at least at one value of the energy. The latter is the weaker necessary condition for S-bend to occur in the caloric curve than that obtained earlier. [S1063-651X(99)09611-7]

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Many efforts have been devoted to the study of structural and thermodynamic properties of the finite systems such as clusters [1–10]. It was shown that the microcanonical caloric curve of the finite system can have a region where a temperature decreases with an energy increase [11–17]. This region is usually named a van der Waals type loop or S bend. Calculations of the energy density of states from the first principles using a histogram Monte Carlo approach leave little doubt about the reality of such a loop [18–22]. The loop is usually related to the coexistence of liquidlike and solidlike states of the finite system. The sufficient conditions for such a loop to occur in the caloric curve have been obtained from various model partition functions in [23–29]. The necessary conditions are now also known [30–32].

The entropy $S(E)$ of the finite system consisting of N particles in the volume V with the total energy E is usually determined by

$$S(E)=k\ln[\rho(E)/\rho_0], \tag{1}$$

where k is the Boltzmann constant and $\rho(E)$ is the energy density of states of the system [19,26,30–32]. Here we choose the reference level for the density of states as a density of unity, so ρ_0 is equal to one state per unit of energy.

The exact relation is given by relating adiabatic invariant phase volume $G(E)$ to the entropy via Boltzmann relation [33–35]

$$S(E)=k\ln G(E). \tag{2}$$

The temperature is given by the thermodynamic relation

$$T(E)=1/[\partial S(E)/\partial E]_{N,V}. \tag{3}$$

The relation (1) and the temperature T_T defined by Eqs. (1) and (3) are approximate for finite systems and become exact in the thermodynamic limit when $N\rightarrow\infty, V\rightarrow\infty, N/V=\text{const}$ [33–35]. Therefore T_T is named the thermodynamic temperature [23]. As shown below in the present study the temperature T_K obtained from Eqs. (2) and (3) can be defined via the mean kinetic energy, therefore T_K is named the kinetic temperature. The difference between the thermodynamic and kinetic temperatures is increased with a decrease in the number of degrees of freedom and becomes great for the system with one degree of freedom. For example for the particle in one dimensional Morse potential well the energy density of states is given [36,37] by

$$\rho(E)=a/\sqrt{1-E/\varepsilon}, \tag{4}$$

where $a=\text{const}$ and ε is the depth of the potential well. Using Eqs. (1)–(4) and the relation

$$\rho(E)=[\partial G(E)/\partial E]_{N,V} \tag{5}$$

we obtain

$$T_T(E)=\frac{2\varepsilon}{k}(1-E/\varepsilon),$$

$$T_K(E)=\frac{2\varepsilon}{k}[\sqrt{1-E/\varepsilon}-(1-E/\varepsilon)].$$

It is easy to see that the properties of T_K and T_T are different in interval $[0;\varepsilon)$. T_T monotonically decreases from $2\varepsilon/k$ to

0 in this interval. T_K increases from 0 to $\varepsilon/2k$ in $[0;\frac{3}{4}\varepsilon)$, and has a maximum equal to $\varepsilon/2k$ at $E=\frac{3}{4}\varepsilon$, and decreases in $(\frac{3}{4}\varepsilon;\varepsilon)$.

Clusters with no center-of-mass motion and zero angular momentum are usually considered in the molecular dynamics (MD) simulations. The energy density of states and the phase volume are given for them by [26,30]

$$\rho(E)=c\int_0^E (E-U)^{s/2-1}\rho_c(U)dU,$$

$$G(E)=\frac{2c}{s}\int_0^E (E-U)^{s/2}\rho_c(U)dU, \tag{6}$$

where $c=\mathrm{const}$, U is the potential energy, $\rho_c(U)$ is the configurational density of states, and $s=3N-6$ is the total number of degrees of freedom.

The probability distribution function of the kinetic energy $E_K(E_K=E-U)$ is determined by

$$\begin{aligned} f(E_K)&=c(E-U)^{s/2-1}\rho_c(U)/\rho(E)\\ &=cE_K^{s/2-1}\rho_c(E-E_K)/\rho(E). \end{aligned}\tag{7}$$

From Eqs. (2), (3), (6), and (7) we have for the mean kinetic energy

$$\begin{aligned} \langle E_K\rangle(E)&=\int_0^E f(E_K)E_K dE_K\\ &=c\int_0^E (E-U)^{s/2}\rho_c(U)dU/\rho(E)\\ &=c\int_0^E E_K^{s/2}\rho_c(E-E_K)dE_K/\rho(E)\\ &=\frac{s}{2}\,\frac{G(E)}{\rho(E)}=\frac{s}{2}\left(\frac{\partial \ln G(E)}{\partial E}\right)_{N,V}=\frac{s}{2}kT_K(E). \end{aligned}$$

It is the mean kinetic energy that must be obtained if the conditions corresponding to the hypothesis of equal *a priori* probabilities are provided in the MD simulations. Therefore the kinetic temperature can be obtained from the MD simulations via relation

$$T_K(E)=\frac{2\langle E_K\rangle(E)}{ks}.$$

We shall show that if the caloric curve $T_K(E)$ has a van der Waals type loop, then the caloric curve $T_T(E)$ has also such a loop, and the reverse statement is not correct.

Let us assume that the energy density of states $\rho(E)$ is the function with smooth first derivative. For convenience we shall not write indices of the derivatives.

From Eqs. (1)–(3) and (5) we have the following relations:

$$T_T^{-1}(E)=\frac{\partial \ln \rho(E)}{\partial E}=\frac{\partial}{\partial E}\left[\ln\left(\frac{\partial G(E)}{\partial E}\right)\right]=\frac{\partial^2 G(E)}{\partial E^2}\Bigg/\frac{\partial G(E)}{\partial E},$$

$$T_K^{-1}(E)=\frac{\partial \ln G(E)}{\partial E}=\frac{\partial G(E)}{\partial E}\Bigg/ G(E),$$

$$\frac{1}{T_K(E)}\,\frac{\partial T_K(E)}{\partial E}=\frac{1}{T_K(E)}-\frac{1}{T_T(E)}, \tag{8}$$

$$T_T(E)=T_K(E)\Bigg/\left(1-\frac{\partial T_K(E)}{\partial E}\right). \tag{9}$$

Equation (9) gives $\partial T_K(E)/\partial E<1$ for $T_K(E)>0$ and $T_T(E)>0$.

By differentiating Eq. (9) we can obtain

$$\begin{aligned} \frac{\partial T_T(E)}{\partial E}&=\frac{\partial T_K(E)}{\partial E}\Bigg/\left(1-\frac{\partial T_K(E)}{\partial E}\right)\\ &\quad+T_K(E)\frac{\partial^2 T_K(E)}{\partial E^2}\Bigg/\left(1-\frac{\partial T_K(E)}{\partial E}\right)^2. \end{aligned}\tag{10}$$

Let us assume that the caloric curve $T_K(E)$ has a van der Waals type loop (Fig. 1). Then we have

$$E_1<E_c<E_2,$$

$$T_K(E_1)>T_K(E_c)>T_K(E_2),$$

$$\begin{aligned} &\frac{\partial T_K(E)}{\partial E}>0 \quad \text{at} \quad E<E_1 \quad \text{and} \quad E>E_2,\\ &\frac{\partial T_K(E)}{\partial E}<0 \quad \text{at} \quad E_1<E<E_2,\\ &\frac{\partial T_K(E)}{\partial E}=0 \quad \text{at} \quad E=E_1 \quad \text{and} \quad E=E_2; \end{aligned}\tag{11}$$

and

$$\begin{aligned} &\frac{\partial^2 T_K(E)}{\partial E^2}<0 \quad \text{at} \quad E<E_c,\\ &\frac{\partial^2 T_K(E)}{\partial E^2}>0 \quad \text{at} \quad E_c<E,\\ &\frac{\partial^2 T_K(E)}{\partial E^2}=0 \quad \text{at} \quad E=E_c. \end{aligned}\tag{12}$$

From Eqs. (8), (9), and (11) we have

$$T_T(E_1)=T_K(E_1) \quad \text{and} \quad T_T(E_2)=T_K(E_2),$$

$$T_T(E)>T_K(E) \quad \text{at} \quad E<E_1 \quad \text{and} \quad E>E_2,$$

$$T_T(E)<T_K(E) \quad \text{at} \quad E_1<E<E_2.$$

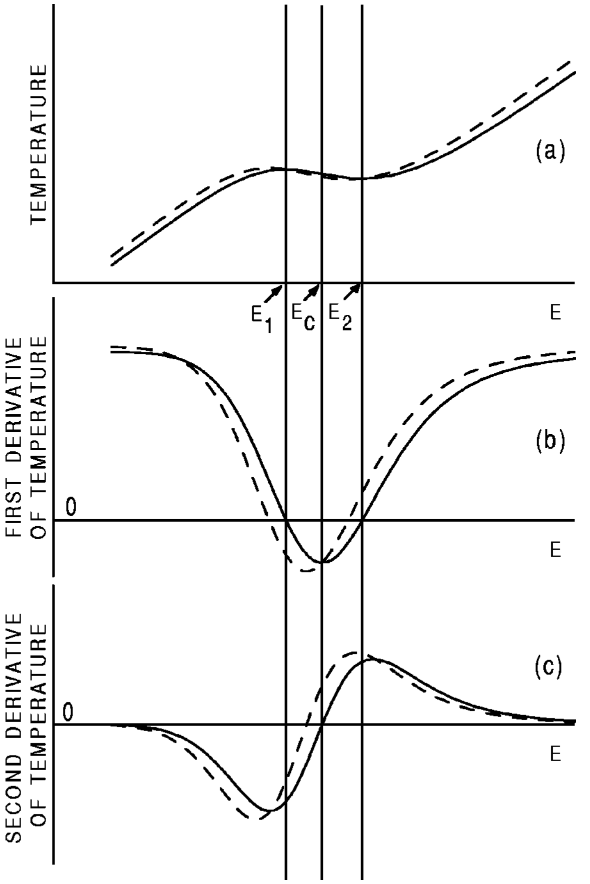

FIG. 1. (a) Microcanonical caloric curves; (b) first, and (c) second derivatives of the microcanonical temperature vs energy. Solid lines correspond to the kinetic temperature and dashed lines to the thermodynamic temperature.

Relations (8)–(12) give

$$\frac{\partial T_T(E)}{\partial E}<0 \quad \text{at} \quad E_1<E<E_c,$$

$$\frac{\partial T_T(E)}{\partial E}>0 \quad \text{at} \quad E>E_2.$$

We take into account that the practically interesting systems usually have the global minima on the potential energy surface and their behavior at low energies can be described by the system of independent harmonic oscillators. The inequality $(\partial T_T(E)/\partial E)_{E=0}>0$ is true for this system. Therefore the caloric curve $T_T(E)$ has also a van der Waals type loop. From the above consideration one can also conclude that the necessary conditions for a loop in the caloric curve $T_T(E)$ can be taken as the necessary conditions for a loop in the caloric curve $T_K(E)$.

Note that the region where $\partial T_T(E)/\partial E<0$ lies lower in the energy axis than the region where $\partial T_K(E)/\partial E<0$.

Following [26], it is easy to show that the stable equilibrium corresponds to $\partial T_K(E)/\partial E>0$, and the instability corresponds to $\partial T_K(E)/\partial E<0$.

When the caloric curve for the thermodynamic temperature has a van der Waals type loop, the caloric curve for the kinetic temperature cannot have such a loop. It is enough to consider the following example in order to prove the above statement.

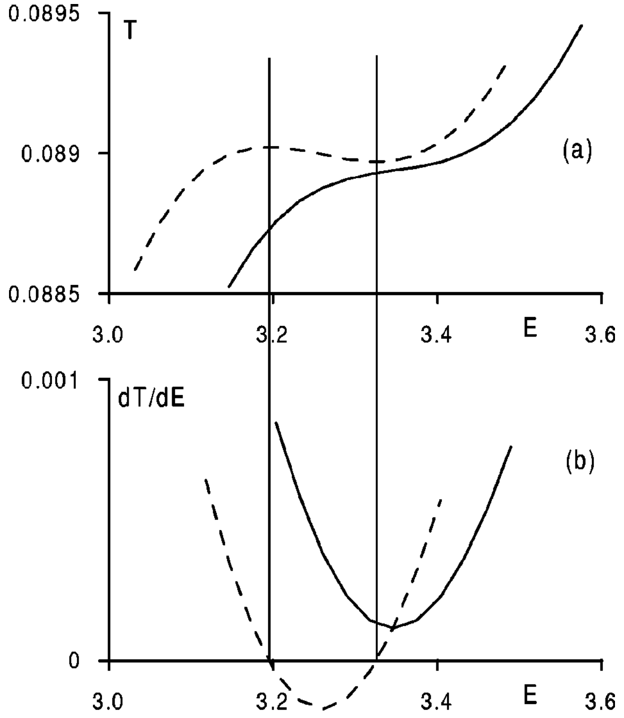

FIG. 2. (a) Microcanonical thermodynamic and kinetic temperatures vs energy for basic model of Ref. [23] with $A=60\,000,D=3.5,s=33$. (b) Derivatives of the temperatures vs energy E. Solid lines correspond to the kinetic temperature and dashed lines to the thermodynamic temperature. Energy is measured in units of D, and the temperatures are measured in units of D/k.

The energy spectrum of the cluster is defined by the distribution of energies of the local minima of the cluster potential energy surface. Each of these energy minima corresponds to an ''inherent structure'' of the cluster [8,9,23]. The basic model of Bixon and Jortner [23] assumes a harmonic approximation for potential wells, and the energy gap, D, between ground state inherent structure and exited ones considerably exceeds the energetic spread of the energies of the exited inherent structures. For the basic model the density of states is given by

$$\rho(E)=B[E^{s-1}+A(E-D)^{s-1}\theta(E-D)],$$

where A and B are constants, s is the number of degrees of freedom, and $\theta(x)$ is the step-function. From Eqs. (1)–(3) and (5) one can see that the caloric curve for the thermodynamic temperature $T_T(E)$ has a van der Waals type loop and the caloric curve for the kinetic temperature $T_K(E)$ has no such loop for $s=33$, $A=60\,000$, $D=3.5$, and an arbitrary B (Fig. 2).

The canonical energy distribution function is defined as a product of the energy density of states and the Boltzmann's exponent [31]. As mentioned above the systems under consideration usually have the global minima on the potential energy surface and their behavior at low energies can be described by the system of independent harmonic oscillators. The behavior of the system can be described by the system of free particles at high energies where the interaction energy between particles becomes small comparing to the total energy of the system. From the above consideration we conclude that the energy density of states is described by power laws at low and high energies, and the second derivative of the logarithm of the canonical energy distribution function has a negative value at low and high energies. Therefore, the logarithm of the canonical energy distribution function has at least two inflection points if the second derivative of the logarithm of the canonical energy distribution function has a positive value at least at one value of the energy.

In [31,32] various equivalent necessary conditions have been obtained for a van der Waals type loop to occur in the caloric curve for the thermodynamic temperature $T_T(E)$. One of these conditions requires that the logarithm of the canonical energy distribution function should have two inflection points. It was noted above that we can take the necessary conditions for S-bend in the caloric curve $T_T(E)$ as the necessary conditions for S-bend in the caloric curve $T_K(E)$. Therefore, we conclude that the necessary condition for S-bend in the caloric curves $T_T(E)$ and $T_K(E)$ requires a positive value of the second derivative of the logarithm of the canonical total energy distribution function at least at one value of the energy. The latter is the weaker necessary condition for S-bend to occur in the caloric curve than that obtained in [31,32].

We have proved that the caloric curve for the thermodynamic temperature has **S**-bend if the caloric curve for the kinetic temperature has S-bend, and the reverse statement is not correct. Using properties of the finite system at low and high energies we have shown that S-bend in the caloric curve of the finite system requires a positive value of the second derivative of the logarithm of the canonical total energy distribution function at least at one value of the energy.

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