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SEPARABILITY OF SPECIFIC VOLUME IN THERMODYNAMIC EQUATION OF STATE*

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A type of system, in which the specific volume can be divided into several parts according to its Hamiltonian, has been obtained in a grand ensemble. The main character of such a system is that its Hamiltonian is absolutely separable. We also discuss the partial specific volume contributed by thermoelectrons in metals under a free-interaction approximation, and the corresponding Wu–Jing parameter is obtained as a simple example.

Keywords: equation of state, high-pressure physics, grand ensemble, Wu–Jing parameter
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I. INTRODUCTION

In a traditional trinomial theory of equation of state (EOS), pressure is taken as a function of specific volume and temperature, which is always separated into a cold part (contributed by crystal lattices and electrons at zero-Kelvin) and a thermal part (contributed by thermoelectrons and crystal-lattice vibrations) in order to determine the EOS conveniently. The validity of this method has been proved in some complicated problems.[1−3] But it is not always true, especially in porous materials with ultra-low initial densities or in high compression-ratio experiments of condensed matters,[4−6] where the pressure, as a function of specific volume and temperature, is of multivalue and inaccuracy magnifying if calculating the corresponding Hugoniot (or isentropic) curve via Mie–Grüneisen EOS.[1,4−6] Therefore, it is necessary to discover a new EOS, in which the pressure is treated as an independent variable and the specific volume is a function of pressure and temperature, similar to that of pressure in a traditional EOS.[4−6] Then the bugs of multivalue and inaccuracy magnifying are eliminated. It is crucial for determining the EOS of some materials that will be dilatable at high pressures.[7−9]

The difficulty for establishing such a theory is that all physical models presented by now are on the basis that all particles move in a certain space, the volume of which is being studied. And this implies that the specific volume has been taken as an independent variable. Hence all models and corresponding functions are inapplicable to the new EOS. The purpose of this paper is to introduce a method, called variable interchanging, to revive these models.

Interchanging the independent variables of EOS should preserve the consistency of the theory both in thermodynamics and in statistical mechanics. Since the system is divided into several parts according to the composition of the Hamiltonian in a traditional theory,[1−3] we must follow it in the new theory, or else we cannot continue. Before discussing this problem in detail, it is helpful to understand what the partial specific volume means. In thermodynamics, pressure is an intensive parameter and can be written as a sum of all partial pressures. So we can freely separate the pressure, leaving other thermodynamic variables and characteristic functions untouched. But the same picture becomes unclear when the same method is used on the specific volume in a new theory, for the specific volume is an extensive parameter and is the space for particles to move. In this sense, not only the characteristic functions but also some thermodynamic variables, for example, the pressure, will depend on the size of the specific volume. What we can do is just to separate the specific volume formally and mathematically. Since not all of the separated specific volumes have explicit counterparts in a realistic model, the specific volume V_i in the following discussion cannot be understood as the specific vol-

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ume of the ith sub-system, but the increment of the total specific volume when taking account of the corresponding sub-system. This method is imperfect from the viewpoint of physics. But considering that it is established directly on a grand ensemble, and the mathematical separation of specific volume leaves the total characteristic functions unchanged, we take the point of view that the following mathematical approach is reasonable and acceptable.

Ⅱ. SEPARABILITY OF SPECIFIC VOLUME

We first consider a system with a two-part Hamiltonian. Its internal energy is divided into two parts, for example, a cold part and a thermal part, i.e. $E = E_{\rm c}+E_{\rm n}$. And the pressure is, analogously, divided into $P_{\rm c}$ and $P_{\rm n}$. Then the enthalpy of this system becomes

$$\begin{aligned} H =& E + PV = E_{\rm c} + P_{\rm c}V + E_{\rm n} + P_{\rm n}V \\ =& H_{\rm c} + H_{\rm n}, \end{aligned} \tag{1}$$

which also has two parts. In principle, using thermodynamic relation $V = \left(\dfrac{\partial H}{\partial P}\right)_{\rm s}$, one can obtain the cold and the thermal parts of the specific volume of this system. Here the subscript 's' means the calculation is done along the isentropic path. But this calculation cannot always be accomplished, because of the partial pressure $P_{\rm c}$ (or $P_{\rm n}$) in the sub-enthalpy $H_{\rm c}$ (or $H_{\rm n}$) in Eq.(1). In fact, we can avoid this difficulty by the following judgment.

Theorem There is a kind of system whose partial specific volumes are calculable. The characters of such a system are as follows. Firstly, the separated sub-Hamiltonians of the system should be absolutely independent, that is, no interactions exist among the particles belonging to different sub-systems. And secondly, the particle number of each sub-system is conservative.

We will prove this theorem in a grand ensemble by a statistical mechanics method. For this purpose, an assumption should be put forward first that the Hamiltonian of the system being studied must be written as

$$H(x_i^{\mu}) = \sum_{i=1}^{n} H_i(x_i), \tag{2}$$

and

$$x_i \cap x_j = \phi \qquad (i \neq j), \tag{3}$$

where ϕ is the null set, x_i^{μ} is the set of the canonical coordinates as i=1,2,3,..., and μ=1,2,..., and x_i the subset of x_i^{μ} as μ=1,2,3,.... On the other hand, the pressure equation in a grand ensemble is[2]

$$PV = \kappa T\zeta = \kappa T \ln \Xi, \tag{4}$$

where the grand partition function Ξ can be written as $\Xi = {\rm e}^{\zeta} = \sum\limits_{N=0}^{\infty} {\rm e}^{-N\alpha} Z_N$ under a condition that the system is chemical pure. Here Z_N is the partition function of this system with N particles, which satisfies

$$Z_N = \frac{1}{N!(2\pi\hbar)^{3N}} \int {\rm e}^{-\beta H} ({\rm d}p{\rm d}q)^N. \tag{5}$$

When introducing these equations (Eqs.(2)–(5)) into a system with an absolutely separable Hamiltonian, we acquire the grand partition function as[2]

$$\Xi = {\rm e}^{\zeta} = \sum_{N_i=0}^{\infty} \prod_{i=1}^{n} {\rm e}^{-N_i\alpha_i} Z_{N_i}, \tag{6}$$

where

$$Z_{N_i} = \frac{1}{N_i!(2\pi\hbar)^{3N_i}} \int {\rm e}^{-\beta H_i} ({\rm d}p{\rm d}q)^{N_i}. \tag{7}$$

Here N_i is the particle number of the sub-system i. Furthermore, Eq.(6) can be simplified as $\Xi = \prod\limits_i \Xi_i = \prod\limits_{i=1}^{n} {\rm e}^{-N_i\alpha_i} Z_{N_i}$ by taking account of the particle number conservation of each sub-system. Thus, a comprehensible form of the pressure equation reads

$$PV = \kappa T \ln \Xi = \sum_i \kappa T \ln \Xi_i. \tag{8}$$

This simple character of addition in Eq.(8) ensures the separability of specific volume. Because there are no partial pressure or specific volumes existing apparently on the right-hand side of Eq.(8), the variable-interchanging mentioned before can be done easily. One of the equivalent forms of Eq.(8) is

$$V = \frac{1}{P}\sum_i \kappa T \ln \Xi_i = \sum_i V_i.$$

In this equation

$$V_i = \frac{\kappa T}{P} \ln \Xi_i \tag{9}$$

is the increment of the total specific volume of the system when sub-system i is taken into account. On the other hand, the pressure equation of sub-system i may be derived from the separability of the total Hamiltonian as

$$P_i V = \kappa T \ln \Xi_i. \tag{10}$$

Hence the total specific volume can be expressed as

$$V = \frac{1}{P_i}\kappa T \ln \Xi_i. \tag{11}$$

Dividing Eq.(11) by Eq.(9), the following relation is obtained

$$V_i/V = P_i/P. \tag{12}$$

The variables in these equations (Eqs.(9)–(11)) are the pressure in Eq.(11) which is the partial pressure, and that in Eq.(9) which is the total pressure. The specific volume is similar. It is suggested from Eq.(12) that for a system with absolutely separated Hamiltonians in a state with pressure P and specific volume V, the ratio of V_i, (the increment of the specific volume regarding sub-system i) to the total volume, equals the ratio of P_i (the partial pressure of sub-system i) to the total pressure.

Besides, it is necessary to point out that Eq.(12) is valid just when $P \neq 0$. The new EOS is obtained completely by using Eq.(9), whose status is similar to the pressure in a traditional trinomial EOS. As a supplement we should further point out that the calculations of the partial specific volume may not be based on the thermodynamic relation mentioned at the beginning of this section but, for simplicity based on Eq.(12) directly.

In this way, we have proved the theorem precisely in a grand ensemble. Of course, there may be other cases, in which the separated specific volume can be calculated, and which are not excluded by this theorem. In fact, the specific volume of crystal lattices is also calculable when using a Debye approximation. But its Hamiltonian is not absolutely separated and is out of the applicability of this theorem. We prefer to discuss this subject in another paper.[10]

Ⅲ. APPLICATION: SPECIFIC VOLUME OF THERMOELECTRONS

We have written the specific volume of a system as a function of pressure and temperature by introducing Eq.(9) into a traditional EOS. In this section, a contribution of the thermoelectrons in metals to specific volume will be discussed as a brief example. As a multiparticle system, crystals are composed of atoms and extra-nuclear electrons. But it is very difficult to solve the motion equations of this system, i.e. a group of Schrödinger equations, which involve the movements of atoms, electrons, and the interactions among these particles, accurately. However, by adopting a Born–Oppenheimer approximation,[11,12] it has been proved that the Hamiltonian of crystals can be divided into two parts: one for electrons and the other for lattices.[13] The interactions between them are taken as perturbations.

In metals, these perturbations can be ignored in a much simpler approximation,[2] which is to take the extra-nuclear electrons as a kind of free Fermi gas moving in a square potential trap with an infinite depth. By this assumption, the electrons and the crystal lattices in this system become independent of each other absolutely. Furthermore, the particle numbers of these two sub-systems are also fixed when shock temperature has tended to a stable value in a final shock state. Therefore, this system meets the conditions of the theorem. Thus, by making use of Eq.(12), one can obtain

$$P_{\rm e}V = PV_{\rm e}, \tag{13}$$

where variables with subscript 'e' belong to the subsystem of thermoelectrons, and others are of the primary system. In a theory on the subject of a free-electrons gas, there is a relation[1−3]

$$P_{\rm e}V = \frac{2}{3}E_{\rm e}, \tag{14}$$

where the partial internal energy

$$E_{\rm e} = N\kappa T \frac{I_{3/2}(\xi)}{I_{1/2}(\xi)}$$

is contributed by thermoelectrons. Substituting Eq.(14) into Eq.(13) yields the partial specific volume of thermoelectrons as

$$V_{\rm e} = \frac{2}{3P}E_{\rm e}. \tag{15}$$

On the other hand, the internal energy of an electron system at low temperature is (where the cold energy and the cold specific volume of electrons at zero-Kelvin have been merged into the cold part of crystals)

$$E_{\rm e} = \frac{1}{2}\beta T^2. \tag{16}$$

Then the specific volume and the enthalpy become as

$$V_{\rm e} = \frac{\beta}{3P}T^2, \tag{17}$$

and

$$H_{\rm e} = E_{\rm e} + PV_{\rm e} = \frac{5}{6}\beta T^2 = \frac{5}{3}E_{\rm e}. \tag{18}$$

Comparing Eq.(18) with Eq.(15) gives the Wu–Jing parameter[5] of thermoelectrons at low temperature as

$$R_{\rm e} = \frac{2}{5}. \tag{19}$$

The parameter β in the above equations is the coefficient of electronic specific heat that satisfies $\beta = \frac{\pi^2 N \kappa^2}{2\mu^0}$. Its value can be determined by a numerical calculation or by experiments directly.

Thus, we have obtained some primary properties of the new EOS for thermoelectrons in metals, where the pressure is taken as an independent variable. We believe that this kind of treatment should be helpful to simplify further calculations about the properties of condensed matters under high pressures.

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