Melting curve of systems with a homogeneous potential function

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We use a scaling transformation of canonical variables which conserves the geometric relations on the phase trajectory of a Hamiltonian N-body system with a homogeneous potential function to obtain the phase equilibrium curves (especially the melting curve) and the dependence of the self-diffusion coefficient on the melting temperature. We show that there are no critical points on the phase equilibrium curve for systems with a homogeneous potential function.

It is well known that the melting curve of normal substances can be very accurately described by the empirical Simon equation:[1–3]

$$P=AT^C+B. \tag{1}$$

A number of papers[4–7] have been devoted to the theoretical justification of this equation. The present paper proposes what would seem to be the simplest, previously unknown, approach to this (and not only this) problem. A hint of the possibility of the proposed method can be found in Ref. 8.

We consider a system of N particles interacting through a potential function $U(\mathbf{r}_1,...,\mathbf{r}_N)=U(q_i)$, where i runs from 1 to $3N$. The classical dynamics will then be governed by the following Hamiltonian equations with $H=K(p_i)+U(q_i)$, where $K(p_i)=\Sigma p_i^2/2m_i$:

$$\frac{dp_i}{dt}=-\frac{\partial U}{\partial q_i}, \quad \frac{dq_i}{dt}i=\frac{\partial K}{\partial p_i}, \quad i=1,...,3N. \tag{2}$$

We assume that $U(q_i)$ is a homogeneous function of degree s: $U(aq_i)=a^sU(q_i)$. We note that $K(p_i)$ is a homogeneous function of degree two: $K(ap_i)=a^2K(p_i)$.

We assume that there exists a solution of (2): $q_i=q_i(t)$, $p_i=p_i(t)$ such that the phase trajectory corresponds to a macrostate which is an equilibrium multiphase system. We can then associate this macrostate with thermodynamic variables P_0, V_0, T_0. Since we use a microcanonical ensemble the pressure and temperature will fluctuate but in the limit as N, $V\rightarrow\infty$ the procedure we have described will not be open to doubt. We note that we can easily introduce a wall potential by simply adding interaction terms to U of the same degree s, but we shall not clutter up the equations since the final result is independent of these terms.

We carry out the following scale transformation of the canonical variables (if we take the wall potential explicitly into account we must add to (3) a transformation of the wall coordinates):

$$q_i'=aq_i, \quad p_i'=bp_i, \quad t'=ct, \tag{3}$$

where a, b, and c are constants and we require that

$$q_i'=q_i'(t')=aq_i(ct), \quad p_i'=p_i'(t')=bp_i(ct)$$

is also a solution of (2). For this it is necessary that the transformation (3) preserve the form of Eqs. (2). Using the homogeneity of the functions K and U one can easily find the required conditions:

$$b^2=a^s, \quad c^2=a^{2-s}, \tag{3'}$$

where a is an arbitrary positive constant.

We draw attention to the major feature of the transformation (3)—it conserves geometric relations on a phase trajectory, thereby preserving the scaling of the individual trajectories of each of the N particles and, hence, it conserves the multiphase nature of the whole system. Finally we can conclude that the scaling transformation (3) transforms one state on a phase equilibrium curve to another state on the same curve.

The simplest example of a phase equilibrium curve is the two-phase melting curve. We use the well known formulas for the temperature and pressure to obtain it:

$$V=a^3V_0$$

$$T=\frac{2}{3N}\left\langle\sum\frac{p_i^2}{2m_i}\right\rangle \rightarrow T=a^sT_0 \rightarrow V=V_0\left(\frac{T}{T_0}\right)^{3/s} \tag{4}$$

$$P=\frac{NT}{V}-\frac{1}{3V}\left\langle\sum q_i\frac{\partial U}{\partial q_i}\right\rangle \rightarrow P=P_0\left(\frac{T}{T_0}\right)^{1-3/s}. \tag{4'}$$

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The Boltzmann constant k is here taken to be unity and $\langle ... \rangle$ indicates time averaging. The exponent in (4) was known before[9] but other methods were used to obtain it. A noteworthy feature of the proposed method is that any physical quantity $F=\langle (q_i, p_i, t) \rangle$ can be represented along the melting curve similarly to (4). For instance, the self-diffusion coefficient is connected with the velocity self-correlation function by the formula

$$D=\frac{1}{3}\int_0^\infty \overline{\mathbf{v}(0)\mathbf{v}(t)}\,dt.$$

Applying (3) we see that D depends as follows on the melting temperature:

$$D=D_0(T/T_0)^{1/2+1/s}. \qquad (5)$$

It is interesting to note that for hypothetical Coulomb (or gravitational) systems with $[s=-1\ (s>-2)]$ the self-diffusion coefficient decreases with increasing melting temperature, but for systems with a steeper repulsive potential with $(s<-2)$, on the other hand, it increases. Could it possibly follow from this observation that the crystallization and melting of Coulomb systems will be strongly inhibited at high temperatures and that then long-lived metastable states would be probable?

A direct consequence of the scaling transformation (3) and Eqs. (4) is that there is no critical point on the phase equilibrium curve for systems with a homogeneous potential function.

The condition for the homogeneity of the potential U is rather rigid and excludes many physical potentials of physical interest. However, potentials of the form

$$U=\sum_{i<j} u_{ij}, \quad u_{ij}=4\varepsilon_{ij}(\sigma_{ij}/r_{ij})^n, \quad s=-n,$$

satisfy the homogeneity condition so that the method is applicable for dense systems with interparticle potentials which have a homogeneous repulsive part when the attractive part of the potential plays the role of a perturbation superposed on the dominating repulsive part. It is interesting that the result (4) is correct both for spheres with identical sizes $(n=+\infty)$ and for different spheres when the phase equilibrium curves cannot intersect one another. This result is also correct for "soft" spheres with a finite n.

One should emphasize that Eqs. (4) and (5) describe whole families of curves in the (V,T), (P,T), and (D,T) planes depending on the choice of the parameters P_0, V_0, T_0, and D_0. Only the choice of P_0, V_0, T_0, and D_0 corresponding to some state of equilibrium between the phases determines a curve along which phase equilibrium is conserved. In other words, physically only phase equilibrium curves are selected from these families of curves.

It is probable that the largest amount of experimental data on melting in the high pressure and temperature region is available for the inert gases. Moreover, the interatomic potential of the inert gases is the simplest and is known better than the interatomic potential of other substances. This is the reason why we chose the inert gases as the object for applying our theory. In Fig. 1 we give the experimental data for the dependence of the pressure on the melting temperature in reduced units. For each gas the unit of temperature (energy) was set equal to the depth V_0 of the potential well and the unit of length to the equilibrium distance r_m of the interatomic potential. We used here the following parameters:

	^{4}He	Ne	Ar	Kr	Xe
r_m, (Å)	2.965	3.102	3.76	4.03	4.36
U_0, (°K)	10.79	42.01	140.42	197.29	280.84

The straight line in Fig. 1 is drawn through the two points

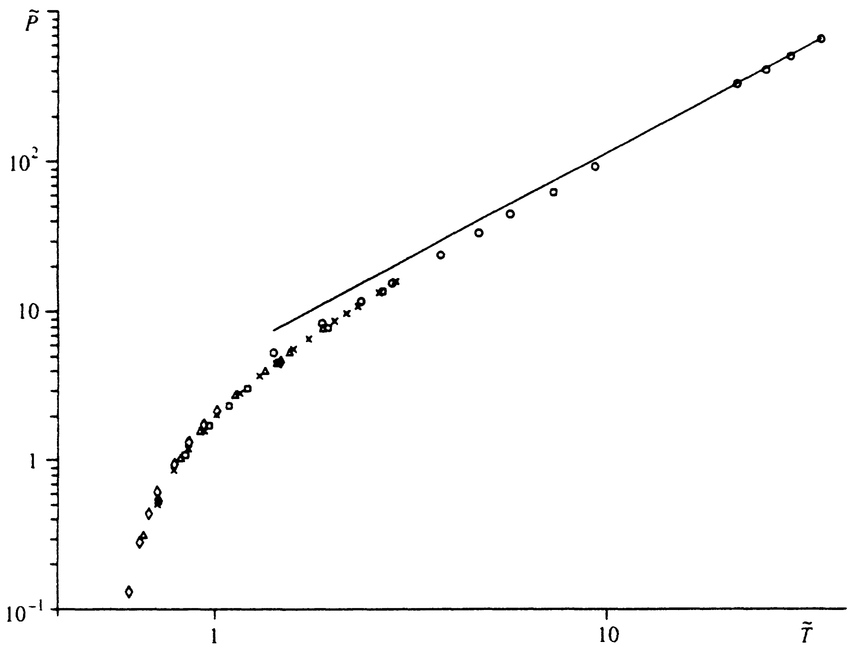

FIG. 1. Dependence of the pressure on the melting temperature of inert gases:[10] ○—^{4}He, □—Ne, ×—Ar, △—Kr, ◇—Xe.

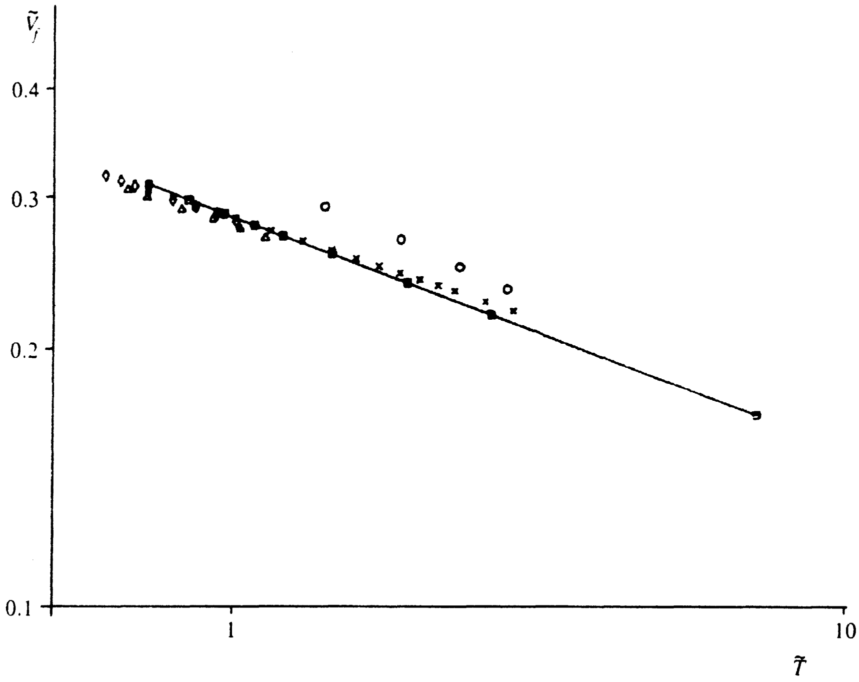

FIG. 2. Dependence of the specific volume in the liquid phase on the melting temperature of inert gases.[10] Notation as in Fig. 1.

with the highest temperatures and corresponds to a repulsive potential with $n_p=6.89$. In Fig. 2 we give the experimental data for the dependence of the specific volume of the liquid phase on the melting temperature in the same units. The straight line in Fig. 2 is drawn through the two points with the highest temperatures and corresponds to a repulsive potential with $n_V=11.41$, i.e., $n_V>n_p$. Qualitatively this result can be explained as follows. The specific volume is proportional to the cube of the average interatomic distance $\bar{r}$ which does not change significantly along the melting curve. One may thus say that the magnitude of the specific volume is sensitive to a change of the potential over a small range of distances over which the potential is approximately homogeneous with index n_V. One readily notes that $n_V=11.41$ is close to $n=12$—the homogeneity index of the repulsive part of the popular interatomic Lennard–Jones potential, $u=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. On the other hand, the pressure depends on the behavior of the potential over much larger ranges of distances over which the potential cannot even approximately be assumed to be homogeneous. To illustrate this statement we consider the equation connecting the pressure in a system with a real potential and the pressure in a system with a homogeneous potential $u_\alpha=4(1/r)^\alpha$ with unknown α ($\varepsilon=1$, $\sigma=1$):

$$P\approx\int_a^\infty g(r)r^3\frac{\partial u}{\partial r}dr=-\int_a^\infty g(r)r^3\left[4\alpha\left(\frac{1}{r}\right)^{\alpha+1}\right]dr. \tag{6}$$

Here $g(r)$ is the radial distribution function, which we put

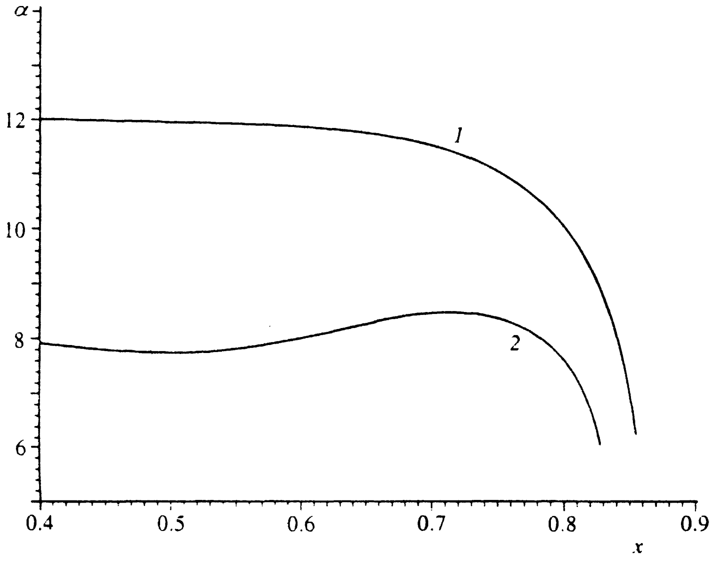

FIG. 3. Dependence of the effective homogeneity index α on the sphere diameter, $x=a/\sigma$, for (*1*) the L–J and (*2*) the B–P potentials.

equal approximately to the first (zeroth) order distribution function of a hard sphere system. In the zeroth approximation we have

$$g(r)=\begin{cases}0, & r\leqslant a,\\ 1, & r>a\end{cases}$$

In the first-order approximation we have

$$g(r)=\begin{cases}0, & r\leqslant a,\\ 1+\frac{4\pi}{3}(\rho a^3)\left(1-\frac{3}{4}\frac{r}{a}+\frac{1}{16}\left(\frac{r}{a}\right)^3\right), & a<r<2a,\\ 1, & r>2a.\end{cases}$$

Here ρ is the density of a system of hard spheres. One finds that the solution of Eq. (6) depends weakly on the form of $g(r>a)$. We show in Fig. 3 the results of a numerical solution of (6) for two interatomic potentials: the Lennard–Jones (L–J) and, more realistically, the Barker–Pomp (B–P) potentials.[11] It is very clear that with increasing density the effective homogeneity index α for the B–P potential becomes approximately constant and satisfies $\alpha\approx 8$, which is much closer to the experimental $n_p=6.89$ than $\alpha=12$ for the L–J potential. One can expect that making the behavior of the interatomic potential at short distances more precise would improve the agreement with experiment even more. Equations (4) thus give a basis for the empirical Simon equation with $C=1-3/s$ both for the case of a homogeneous potential and for a realistic potential with an inhomogeneous repulsive part and an effective homogeneity index α, given by (6), with $C=1+3/\alpha$.

Landau and Lifshitz (see Ref. 12, §31, Probl.1) considered a scaling transformation of the partition function. However, in the opinion of the author, the approach using a partition function leads to the loss of information about the individual motion of each particle in the system and therefore it becomes impossible to use a geometric representation of the motion, which is proposed in the present paper.

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