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Supercritical Grüneisen parameter and its universality at the Frenkel line

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We study the thermomechanical properties of matter under extreme conditions deep in the supercritical state, at temperatures exceeding the critical one by up to four orders of magnitude. We calculate the Grüneisen parameter γ and find that on isochores it decreases with temperature from 3 to 1, depending on the density. Our results indicate that from the perspective of thermomechanical properties, the supercritical state is characterized by a wide range of γ's which includes solidlike values—an interesting finding in view of the common perception of the supercritical state as being an intermediate state between gases and liquids. We rationalize this result by considering the relative weights of oscillatory and diffusive components of the supercritical system below the Frenkel line. We also find that γ is nearly constant at the Frenkel line above the critical point and explain this universality in terms of the pressure and temperature scaling of system properties along the lines where particle dynamics changes qualitatively.

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I. INTRODUCTION

Dimensionless quantities play an important role in describing physical phenomena. One such parameter, the Grüneisen parameter (GP), has been proved to be very useful in the theory of lattice vibrations and thermodynamics of solids. In solid state physics, the GP describes the change in the system's elastic properties in response to volume change [1],

$$\gamma = -\left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T, \tag{1}$$

where ω is the effective average frequency of particle vibrations and V is the system volume. The Grüneisen parameter can also be related to the system energy and pressure [2]:

$$\gamma = V\left(\frac{\partial P}{\partial E}\right)_V. \tag{2}$$

Equations (1) and (2) are equivalent in the condensed matter systems, but the second equation is more general and applies to gases, high-temperature fluids, and plasma where individual particles do not vibrate. Equation (2) leads to [2]

$$\gamma = \frac{\alpha_P B_T V}{C_V}, \tag{3}$$

where α_P is the thermal expansion coefficient, B_T is the isothermal bulk modulus, and C_V is the constant-volume heat capacity.

As follows from (1) and (2), γ is a thermomechanical quantity, which is important for thermomechanical effects, in particular, for those involving extreme temperatures and pressures. These include shock wave effects, rapid expansion, heating of systems absorbing nuclear radiation, and so on. Here, the GP becomes particularly important: if, as is often the case, the pulse duration is shorter than the time scale of acoustic transport, the induced thermal pressure is directly proportional to γ. Consequently, the GP is extensively used in analyzing the equations of state of condensed matter and plasma under extreme conditions.

For most condensed matter systems, the range of γ is 0.5–4. Diamond is an "ideal" Grüneisen system with $\gamma = 1$ [3]. Systems with large pressure derivatives of B (the lattice stiffens quickly with compression) often have large γ [2]. Interestingly, since B_T and C_V are positive in equilibrium, the sign of γ is governed by the sign of α_P. Some systems such as Cu_2O and ScF_3 have a small negative γ over a quite large temperature and pressure range [4], accompanied by a negative α_P and softening of force constants on compression. Negative γ's can also be seen in shock-wave experiments due to nonequilibrium smeared phase transformations [5].

Compared to solids, relatively little is known about the GP in liquids and dense gas states. For the ideal gas, $\gamma = \frac{2}{3}$ is a constant as follows from $E = \frac{3}{2}PV$. The same result also applies to the degenerate electron gas [6]. For the frequently discussed hard-spheres model, γ can be calculated from the Carnahan-Starling equation $Z = \frac{PV}{Nk_BT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$, where $\eta = \frac{\pi}{6}\rho\sigma^3$ is the packing fraction of hard spheres of diameter σ at density ρ [7]. This gives $\gamma = \frac{2}{3}f(\rho)$, where $f(\rho)$ is a function of the density, implying that the GP of hard spheres is constant along isochores. For the model van der Waals system, $\gamma = \frac{2}{3}\frac{V}{V-Nb}$, where b is the cohesion volume, the GP diverges when the volume becomes close to the critical volume [8]. The soft-sphere interaction with weak attraction modifies the GP, and there are analytical evaluations of this effect [9,10]. Based on certain assumptions and in reasonable

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agreement with simulations of noble-gas systems [11], there are numerical evaluations of the GP for the commonly used Lennard-Jones potential [12]. For more complicated liquids such as water and mercury, the GP was calculated using (3) and was found to increase with pressure, in contrast to its usual decrease in crystals [13]. The GP was also calculated in liquid Ar over a small range of pressure and temperature and was found to decrease upon isobaric heating [14]. Over a wider temperature and pressure range, the γ in Ar in the dense gas and liquid state increases upon isothermal compression and is nearly constant upon isochoric heating [15]. γ was also calculated from ensemble averages of fluctuations [16]. Finally, γ was evaluated using the radial distribution function of liquids with acceptable errors [17].

Notably, no studies or evaluations of γ were done significantly above the critical point of matter. Supercritical fluids started to be widely deployed in many important industrial processes [18,19] once their high dissolving and extracting properties were appreciated. Theoretically, little is known about the supercritical state, apart from the general assertion that supercritical fluids can be thought of as high-density gases or high-temperature fluids whose properties change smoothly with the temperature or pressure and without qualitative changes in the properties. This assertion followed from the known absence of a phase transition above the critical point. We have recently proposed that this picture should be modified and that a new line, the Frenkel line (FL), exists above the critical point and separates two states with distinct properties [20–24].

The main idea of the FL lies in considering how particle dynamics changes in response to the pressure and temperature. Frenkel previously proposed that particle dynamics in the liquid can be separated into solidlike oscillatory and gaslike diffusive components and introduced the liquid relaxation time τ as the average time between particle jumps between neighboring quasiequilibrium particle positions [25]. We proposed that this separation applies equally to supercritical fluids and to subcritical liquids: an increasing temperature reduces τ, and each particle spends less time oscillating and more time jumping; an increasing pressure reverses this and results in an increase in the time spent oscillating relative to jumping. An increasing temperature at a constant pressure (or a decreasing pressure at a constant temperature) eventually results in the disappearance of the solidlike oscillatory motion of particles; all that remains is the diffusive gaslike motion. This disappearance represents a qualitative change in particle dynamics and gives a point on the FL. Notably, the FL exists at an arbitrarily high pressure and temperature, as does the melting line. Quantitatively, the FL can be rigorously defined by the pressure and temperature at which the minimum of the velocity autocorrelation function (VAF) disappears [23]. Above the line defined in such a way, the velocities of a large number of particles stop changing their sign and particles lose the oscillatory component of motion. Above the line, the VAF is monotonically decaying as in a gas [23]. Another criterion for the FL, which is important for our discussion of thermodynamic properties and which coincides with the VAF criterion, is $c_v = 2k_B$ [23]. Indeed, the loss of solidlike oscillatory components of motion implies the disappearance of solidlike transverse modes, which, in turn, gives $c_v = 2k_B$ [20]. The qualitative change of particle dynamics and $c_v = 2k_B$ at the FL are two important insights that we use below to discuss the universality of the GP at Frenkel line.

The aim of this paper is to calculate and analyze the GP deep in the supercritical state. We calculate γ for two common model systems at a temperature and pressure exceeding the critical ones by orders of magnitude. We find that γ decreases with temperature from solidlike to gaslike values on isochores. This implies that from the perspective of thermomechanical properties, the supercritical state is characterized by the range of γ which includes the solidlike values. This is an interesting finding in view of the common perception of the supercritical state as being an intermediate state between gases and liquids, which we rationalize in terms of the relative weights of the oscillatory and diffusive components of particle motion. We also find that γ is nearly constant at the Frenkel line in the supercritical state. We explain this universality in terms of pressure and temperature scaling of system properties along the lines where the particle dynamics qualitatively changes.

II. SIMULATION DETAILS

First, we use the molecular dynamics (MD) simulation package DL_POLY [26] to simulate the LJ model. The simulated systems have 8000 particles with periodic boundary conditions and the interatomic potential for argon is the pair LJ potential [27]. We have simulated five densities: $\rho = 1.20$, 1.35, 1.50, 1.90, and 2.20 g/cm^3. The temperature in each simulation varies from the melting temperature at the corresponding density up to 10 000 K at intervals of 10 K. The MD systems were first equilibrated in the *NVE* ensemble for 40 ps. The data were subsequently collected at different temperatures for each density and averaged over a period of 60 ps.

We have also simulated the soft-sphere system over a wide range of density and temperature. The soft-sphere interaction potential is $U(r) = \varepsilon(\frac{\sigma}{r})^n$, where n is the softness parameter. We have considered $n = 6$ and $n = 12$, respectively. For $n = 6$, we performed MD simulations of energy and pressure and calculated γ using Eq. (2). This part of the simulation work was performed using the LAMMPS MD package [36]. A system of 4000 particles in a cubic box with periodic boundary conditions is simulated. The reduced densities of the system are $\rho_1^* = 1.0$ and $\rho_2^* = 1.5$ and the temperatures vary from $T^* = 2.7$ to $T^* = 3.4$ in soft-sphere units. The Frenkel temperature of this system at this density is $T_F^* = 3.1$. The equilibration and production runs involved 10^6 steps with the time step set to 0.0001.

III. RESULTS AND DISCUSSION

We have calculated γ using two methods. In the first method, we use V, P, and E from the MD simulations, calculate γ using Eq. (2), and fit the resulting values to the polynomial. In the second method, we first fit V, P, and E to the respective polynomials and then calculate γ using Eq. (2). Both methods result in close curves for γ as follows from Figs. 1 and 2, discussed below.

We show the γ calculated for Ar using both methods along five isochores in Figs. 1 and 2. We note that the range of

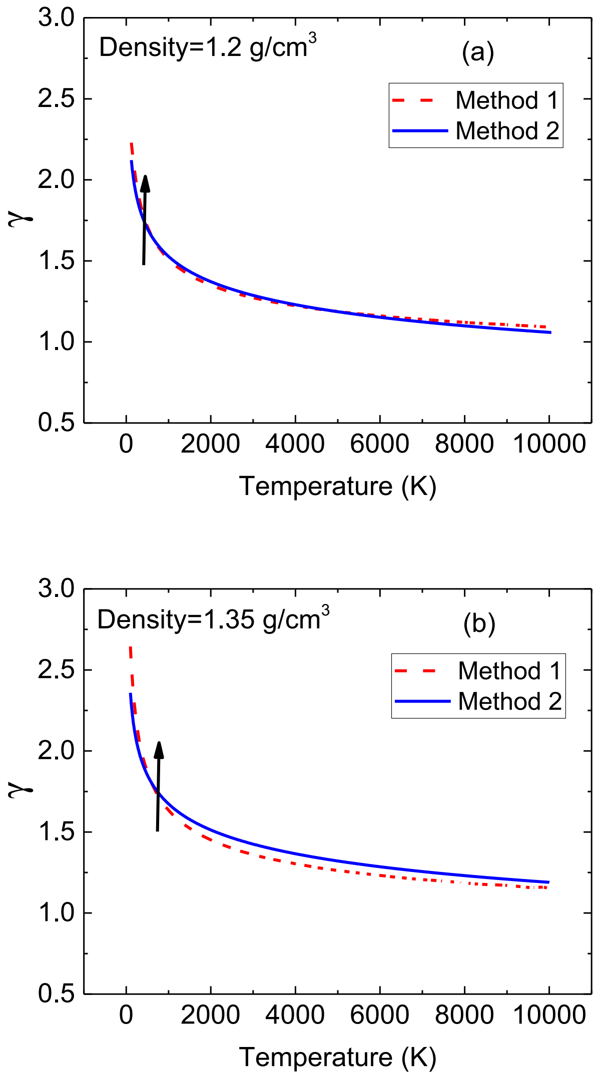

FIG. 1. Grüneisen parameters calculated for the Lennard-Jones (Ar) system at two lower densities. Dashed red lines and solid blue lines are calculated using the two methods described in the text. Arrows show the temperature at the Frenkel line.

thermodynamic parameters we used is a record high: the highest temperature and pressure exceed the critical ones by more than one to two orders of magnitude. At each density, the arrow shows the corresponding temperature of the FL.

We observe that γ calculated by Eq. (2) decreases from 2.5 to 1 with temperature at a low density and from about 3 to 1.2 at a high density. Notably, $\gamma = 2.5$–3.5 is characteristic of the solid state. Therefore, our results indicate that from the perspective of thermomechanical properties, the supercritical state is characterized by a range of γ which includes the solidlike values. This is an interesting finding in view of the common perception of the supercritical state as being an intermediate state between gases and liquids [18,19].

The solidlike values of supercritical γ at low temperatures can be explained by considering the relative weight of the oscillatory and diffusive components of motion in the supercritical state. This weight can be quantified by the R

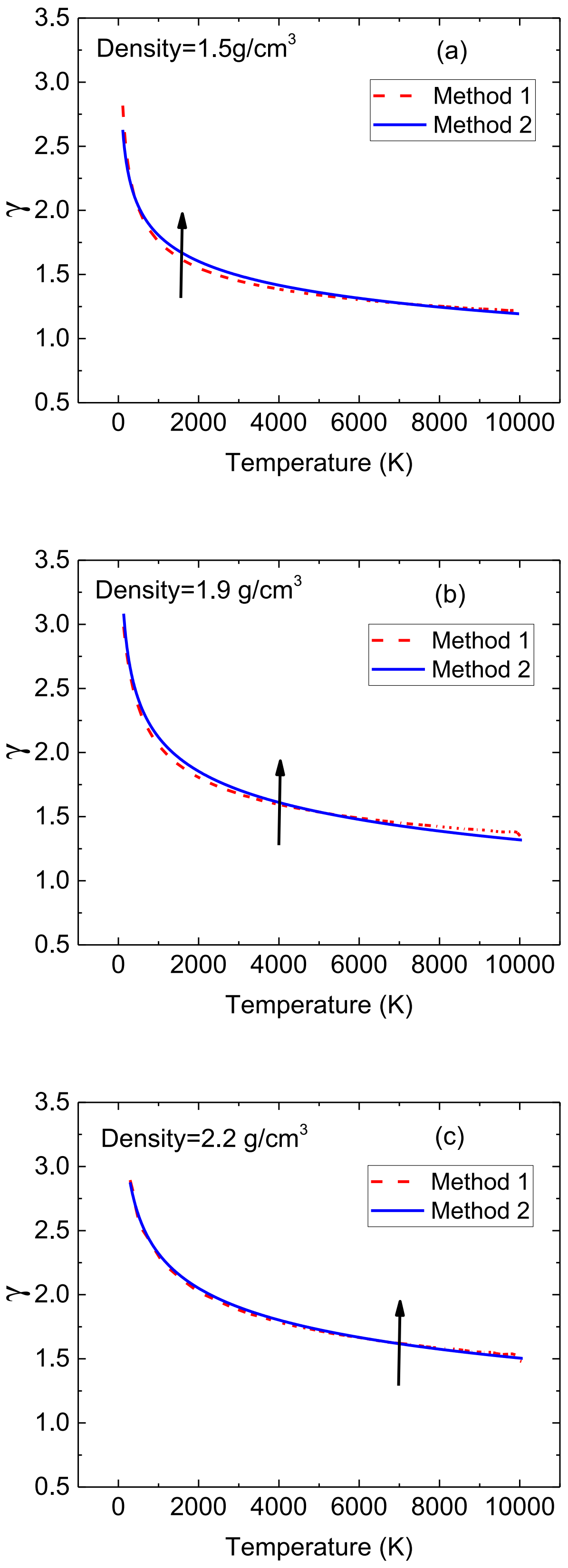

FIG. 2. Grüneisen parameters calculated for the Lennard-Jones (Ar) system at three higher densities. Dashed red lines and solid blue lines are calculated using the two methods described in the text. Arrows show the temperature at the Frenkel line.

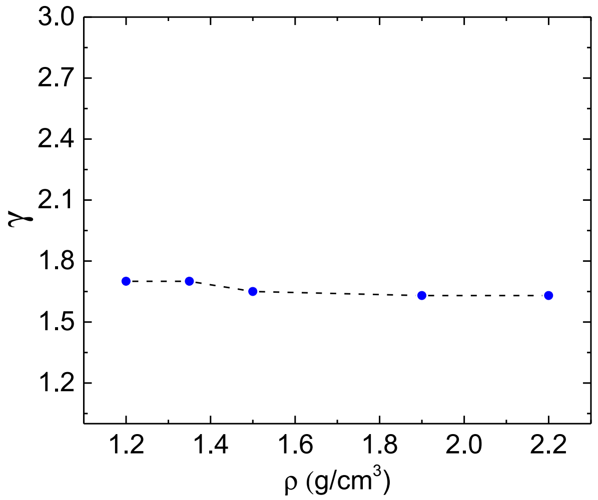

FIG. 3. Grüneisen parameters at the Frenkel line for the five densities used in Figs. 1 and 2. γ values are plotted in the range corresponding approximately to the largest and smallest γ in Figs. 1 and 2.

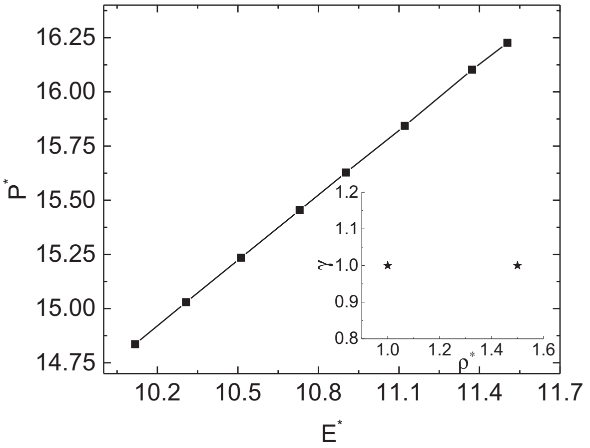

FIG. 4. Dependence of pressure on energy for the soft-sphere system with $n = 6$ at $\rho^* = 1.0$. Pressure and energy are shown in soft-sphere units. Inset: Grüneisen parameter at two densities at the FL: $\rho^* = 1.0$ and $\rho^* = 1.5$.

parameter [20],

$$R = \frac{\omega_F}{\omega_D}, \tag{4}$$

where $\omega_F = \frac{1}{\tau}$ and ω_D is the Debye frequency.

Recall that the oscillatory component of particle motion disappears at the Frenkel line. However, if the supercritical system is sufficiently below the FL, particles spend most of their time oscillating, and diffusive jumps between quasiequilibrium positions are rare. This gives $R \ll 1$. It is easy to show [20] that in this case the average system energy is well approximated by the energy of the oscillatory motion. Therefore, the basic thermodynamic properties of the supercritical system below the FL are solidlike, as are the dynamical properties related to phonons. Hence we expect γ to be characterized by solidlike values in this regime.

We can explore the similarity between the γ values of the supercritical systems below the FL and their solidlike values further by using the solidlike equation, (1). We have earlier evaluated the Debye frequencies ω_D for the LJ system for two supercritical densities below the FL: $\omega_D = 7.2$ THz for $\rho = 1.50$ g/cm^3 and $\omega_D = 18.4$ THz for $\rho = 1.90$ g/cm^3 [28]. Using these values and $\omega \propto \rho^{\gamma}$, which follows from (1), gives $\gamma \approx 3.8$. This is in reasonable agreement with the γ calculated in the MD simulation at a high density, given the approximations involved in finding ω_D.

We now address the behavior of γ at the FL and plot the GP at all five densities and temperatures corresponding to the FL in Fig. 3. γ values are plotted in the range corresponding approximately to the largest and smallest γ in Figs. 1 and 2. We observe that γ is nearly constant at the FL: $\gamma = 1.6$–1.7. This is an interesting result, given that the corresponding temperature at the FL varies by more than an order of magnitude.

We propose the following explanation of the near-constancy of γ at the FL. The universality of γ is related to scaling. At a high energy (e.g., high pressure or temperature), particle interactions mostly involve the repulsive part of the potential. Therefore, the interatomic potential for Ar (as well as for many other systems) becomes effectively close to the soft-sphere potential $U \propto \frac{1}{r^n}$ [29,30], the classic example of a homogeneous potential. According to the Klein theorem [31–33], the nonideal part of the partition function depends on the density ρ and temperature as $\frac{\rho^{\frac{n}{3}}}{T}$ rather than on ρ and T separately. The resulting relationship between temperature and pressure at the melting line is $P_m \propto T_m^{1+\frac{3}{n}}$ [33]. (Interestingly, the kinetic energy is also a homogeneous function of the second order, leading to scaling of kinetic coefficients such as viscosity and diffusion [34,35]). Zhakhovsky extended the scaling argument [35] and noted that, more generally, scaling always exists along those lines in the phase diagram where particle trajectories are similar or change in a way similar to what they do at, for example, the melting line. Recall that the Frenkel line separates the combined oscillatory and diffusive motion below the line from purely diffusive motion above the line [20–24]. Therefore, we expect the scaling relationship $P_F \propto T_F^{1+\frac{3}{n}}$ to hold at the FL as it does at the melting line. Such a relationship has indeed been ascertained in the soft-sphere system as well as the LJ system at high pressures on the basis of MD simulations [23]. Then $\gamma = V\frac{dP}{dE} = V\frac{dP}{dT}\frac{dT}{dE} \propto VT^{\frac{3}{n}}\frac{1}{C_V}$. Using the scaling relationship $V \propto T^{-\frac{3}{n}}$ from the Klein theorem, this gives $\gamma = f(n)\frac{1}{C_v}$, where $f(n)$ is a function of n only. As mentioned earlier, C_v is constant at the FL [20,23]. Hence, γ at the FL does not depend on the temperature and pressure, i.e., it is a universal parameter for a system with a given n.

To compare the results of the scaling argument with MD simulations further, we have calculated γ for the soft-sphere system over a wide range of density and temperature. We show the results for $n = 6$ in Fig. 4 for two densities, $\rho^* = 1.0$ and $\rho^* = 1.5$. Consistent with the scaling argument above (the soft-sphere system obeys the scaling argument) we observe that γ is nearly constant at the FL.

We note that γ for the soft-sphere system at the FL increases with n: using the previous data [37] we calculate γ to be 1.5 for $n = 12$ at the FL. This is close to γ at the FL for the LJ system (see Fig. 3). This can be understood because the LJ potential becomes close to the soft-sphere potential at high pressures and high temperatures as discussed above.

Before concluding, we make two remarks. First, we recall the earlier observation that γ is constant along the isochore [15]. This was related to a narrow range of pressure and temperature in which the system can be approximated by a soft-sphere system with nearly constant effective radii and packing fraction and whose GP is constant along the isochore as mentioned earlier. At the same time, our results involving a large range of pressure and temperature indicate that γ can vary substantially, from values typical of solids to dense-gas values.

Second, it will be interesting to evaluate the GP in the vicinity of the critical point. According to (3), γ is governed by quantities which diverge at the critical point: compressibility, thermal expansion, and heat capacity. Assuming, as is often done in the theory of critical phenomena, that the divergences of α and β_T are equivalent, γ at the critical point is governed by the behavior of C_v. For real systems, C_v has a weak power divergence at the critical point, and γ can be predicted to be close to 0. This point warrants further investigation.

IV. CONCLUSIONS

In summary, we have calculated the Grüneisen parameter of supercritical matter for two model systems over a very wide range of pressure and temperature. We find that γ varies over a wide range which interestingly includes solidlike values. We also find that γ is nearly constant along the Frenkel line and rationalize this finding using the scaling of system properties along the lines where the particle dynamics changes qualitatively. It is likely that a more general statement applies: any dimensionless parameter is universal at the line where scaling operates.

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