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Supercritical phenomenon of hydrogen beyond the liquid–liquid phase transition

Renzhong Li[1], Ji Chen[1], Xinzheng Li[1,2], Enge Wang[1,2] and Limei Xu[1,2]

[1] International Center for Quantum Materials and School of Physics, Peking University, No. 5 Yiheyuan Road, Haidian District, Beijing 100871, People's Republic of China
[2] Collaborative Innovation Center of Quantum Matter, Beijing, People's Republic of China

E-mail: xzli@pku.edu.cn and limei.xu@pku.edu.cn

Abstract

Using *ab initio* molecular dynamics simulation, we investigate the supercritical phenomenon associated with the liquid–liquid phase transition of hydrogen by studying the isothermal response functions, such as electric conductivity, molecular dissociation coefficient and isothermal compressibility, with respect to pressure. We find that, along each isotherm in the supercritical region, each of these response functions shows a maximum, the location of which is different for different response functions. As temperature decreases, the loci of these maxima asymptotically converge to a line of zero ordering field, known as the Widom line along which the magnitude of the response function maxima becomes larger and larger until it diverges as the critical point is approached. Thus, our study provides a possible way to locate the liquid–liquid critical point of hydrogen from the supercritical region at lower pressures. It also indicates that the supercritical phonomenon near the critical point of hydrogen is a rather general feature of second-order phase transition, it is not only true for classical systems with weak interactions but also true for highly condensed system with strong inter-atomic interactions.

Most substances have only one liquid state. Recent studies indicate that a category of substances with anomalous properties, such as water [1], phosphorus [2], and silicon [3], have two liquid states, a low density liquid and a high density liquid. The liquid–liquid phase transition (LLPT) between two liquids and its terminal point—the liquid–liquid critical point (LLCP)—are considered as the origin of different anomalies, such as density anomaly and negatively sloped melting curve, thus have been attracting extensive attentions [4–12]. In these systems, the LLPT and the LLCP are typically buried in deep supercooled region which is difficult to detect in experiment due to crystallization. Recent studies showed that the Widom line, defined as the line of zero ordering field, can be used to trace the LLCP from the supercritical region [7, 11, 13]. This is because the response functions display maxima in the one-phase region, and converge to a single line—the Widom line in the vicinity of the critical point at which all response functions diverge [14].

High pressure hydrogen, which plays a prominent role in planetary science and condensed matter physics, is another example of materials showing indication of LLPT from atomic hydrogen to molecular hydrogen upon cooling along constant pressure [15–18]. According to previous studies [19, 20], the LLCP, if exists, locates at rather high pressure which is difficult to detect experimentally. The question of specific interest here is whether the liquid–liquid critical phenomenon of matters that are highly condensed and have strong inter-atomic interactions can be investigated by tracing the Widom line in supercritical region proposed in classical systems [7, 8]. Particularly, whether the phenomenon of liquid hydrogen, e.g., continuous and discontinuous metallization and dissociation at different phase regions, can be rationalized in terms of the critical and supercritical phenomenon of a second-order critical point.

Using *ab initio* Born–Oppenheimer molecular dynamics (BOMD), we explore the supercritical region of the LLPT in high pressure hydrogen. We investigate the response functions, e.g., isothermal compressibility κ_T, response functions of the direct current (DC) electric conductivity σ and molecular dissociation coefficient f, with respect to pressure in the supercritical region. We find that these response functions show maxima upon

compression along constant temperature, with the maximum for different response functions located at different pressures. As temperature decreases, the loci of these maxima asymptotically approach one another and converge to a single line, resembling the Widom line in the vicinity of the LLCP observed in classical systems [7, 14] below which all response functions diverge. This indicates that the supercritical phonomenon in the vicinity of a LLCP is a rather general feature of second-order phase transition, it is not only true for classical systems with weak interactions but also true for highly condensed systems with strong inter-atomic interactions. In particular, we find that the different phenomenon of hydrogen at high temperatures, e.g., molecular dissociation and continuously metallic transition, are associated with supercritical phenomenon in the vicinity of a LLCP. Meanwhile, it also provides a possible method to experimentally locate the LLCP of hydrogen by tracing the terminal point of the Widom line in supercritical region.

Employing density-functional theory (DFT) and using the Vienna *ab initio* simulation package [21, 22], we perform 'Born–Oppenheimer-type' molecular dynamics (MD) simulations on a supercell containing 250 atoms. A $(2 \times 2 \times 2)$ Monkhorst–Pack grid is employed for the Brillouin zone integration. Its convergence has been checked using $(3 \times 3 \times 3)$ and $(4 \times 4 \times 4)$ grids. Other technical details include: (1) PAW pseudopotentials and an energy cutoff of 500 eV for the expansion of the electronic wave functions, and (2) a 0.5 fs time step employed along with 10 000 steps (5 ps) for each MD simulation. NVT-ensemble with Nosé–Hoover chain is employed in our simulation [23].

Figure 1(a) shows the equation of state of hydrogen based on BOMD simulations for temperature varying from $T = 2000$ to 2500 K. Along isotherms, volume V shows a discontinuous drop at temperatures lower than 2300 K, an indication of the first-order LLPT of hydrogen. For temperatures higher than 2300 K, V is a continuous function of P, indicative of a continuous transition in this region. These are consistent with the simulation results reported in [15] that the system undergoes a first-order transition below 2000 K and shows no evidence of such transition at 3000 K [16].

By calculating the frequency-dependent macroscopic dielectric function (without local field effect) at each snapshot using the Kohn–Sham orbitals [24], we determine the DC electric conductivity σ as the zero frequency limit of the real part of frequency dependent electric conductivity determined by using the following relation derived from the Kubo–Greenwood equation [25, 26], $\sigma(\omega) = \omega \times \frac{\text{Im}\,\epsilon(\omega)}{4\pi}$. Randomly taking 50 snapshots (to ensure a well-sampling of the electric properties) from each BOMD simulation, we calculate the evolution of σ as a function of the pressure along constant temperatures. As can be seen from figure 1(b), similar to the behavior of volume, σ is a discontinuous function of pressure along isotherms $T < 2300$ K, while for $T \geqslant 2300$ K, it shows a continuous increase with pressure, for instance, from a few $(\Omega\ \text{cm})^{-1}$ at 61 GPa to 2600 $(\Omega\ \text{cm})^{-1}$ at 79 GPa for $T = 2500$ K. This sharp increase in the electric conductivity is consistent with the experimental observation of a continuous decrease in the electric resistance by four orders of magnitude from 93 to 140 GPa though at lower pressures [27, 28].

Defining a hydrogen as molecular hydrogen when the distance to its nearest neighbor is less than a certain value $r_c = 0.8$ Å (the first minimum in pair correlation function) and as atomic one otherwise, we characterize the structure change of hydrogen liquid by the fraction of populations of molecular and atomic hydrogen [12]. We denote the fraction of the molecular hydrogen, f (atomic hydrogen, $1 - f$) and present its behavior as a function of pressure along different isotherms in figure 1(c). Similar to the behavior above, the fraction of molecular hydrogen shows discontinuous change along isotherms for $T < 2300$ K, while it changes continuously with increasing pressure for $T \geqslant 2300$ K. This is consistent with the continuous molecular dissociation at high temperatures reported in [15].

To gain more insight to the relation between the continuous and discontinuous transition, we calculate the response functions of thermodynamic, electric and structural properties. These quantities are isothermal compressibility, $\kappa_T \equiv -\frac{1}{V}(\frac{\text{d}V}{\text{d}P})_T$, derivative of electric conductivity $\text{d}\sigma/\text{d}P$ and molecular dissociation coefficient $\text{d}f/\text{d}P$, as shown in figure 2.

We observe three characterics. Firstly, each response function shows a maximum along each isotherm, but the position of the peak shifts to higher pressure as temperature decreases. For instance, κ_T exhibits a maximum at different pressures for different isotherms (figure 2(a)). Upon decreasing temperatures, this peak position shifts to higher pressure, e.g, from $P \sim 72$ GPa at 2500 K to $P \sim 74$ GPa at 2400 K. Similarly, for the DC electric conductivity and molecular dissociation coefficient, their derivatives with respect to pressure $\text{d}\sigma/\text{d}P$ (figure 2(b)) and $\text{d}f/\text{d}P$ (figure 2(c)) also show a peak along each isotherm. Secondly, the magnitude of the peak of each response function increases as temperature decreases and tends to diverge near 2300 K. For instance, the peak of κ_T becomes sharper as temperature decreases from 2500 to 2300 K. Thirdly, for different response functions, the loci of their maxima are different. For example, at 2500 K, the peak position resides at $\sim$68 GPa for $\text{d}\sigma/\text{d}P$ and $\sim$70 GPa for $\text{d}f/\text{d}P$, clearly different from $\sim$72 GPa for κ_T. In addition, such differences in pressure become smaller as the loci of the response maxima converge to one line in the vicinity of 2300 K. The loci of the response function maxima in the supercritical region of the (P, T) phase diagram are shown in

Figure 1. Physical properties such as volume, conductivity and fraction of molecular hydrogen population as a function of pressure. (a) Equation of state for hydrogen along isotherms based on *ab initio* BOMD simulations. A cliff starts to appear in the *V–P* curve as temperature decreases. (b) The dc electronic conductivity calculated using the Kubo–Greenwood formula along *T* = 2000, 2200, 2300, 2400 and 2500 K. (c) Structure changes, the fraction of the molecular hydrogen (filled symbol) and dissociation coefficient (open symbol), along constant temperature.
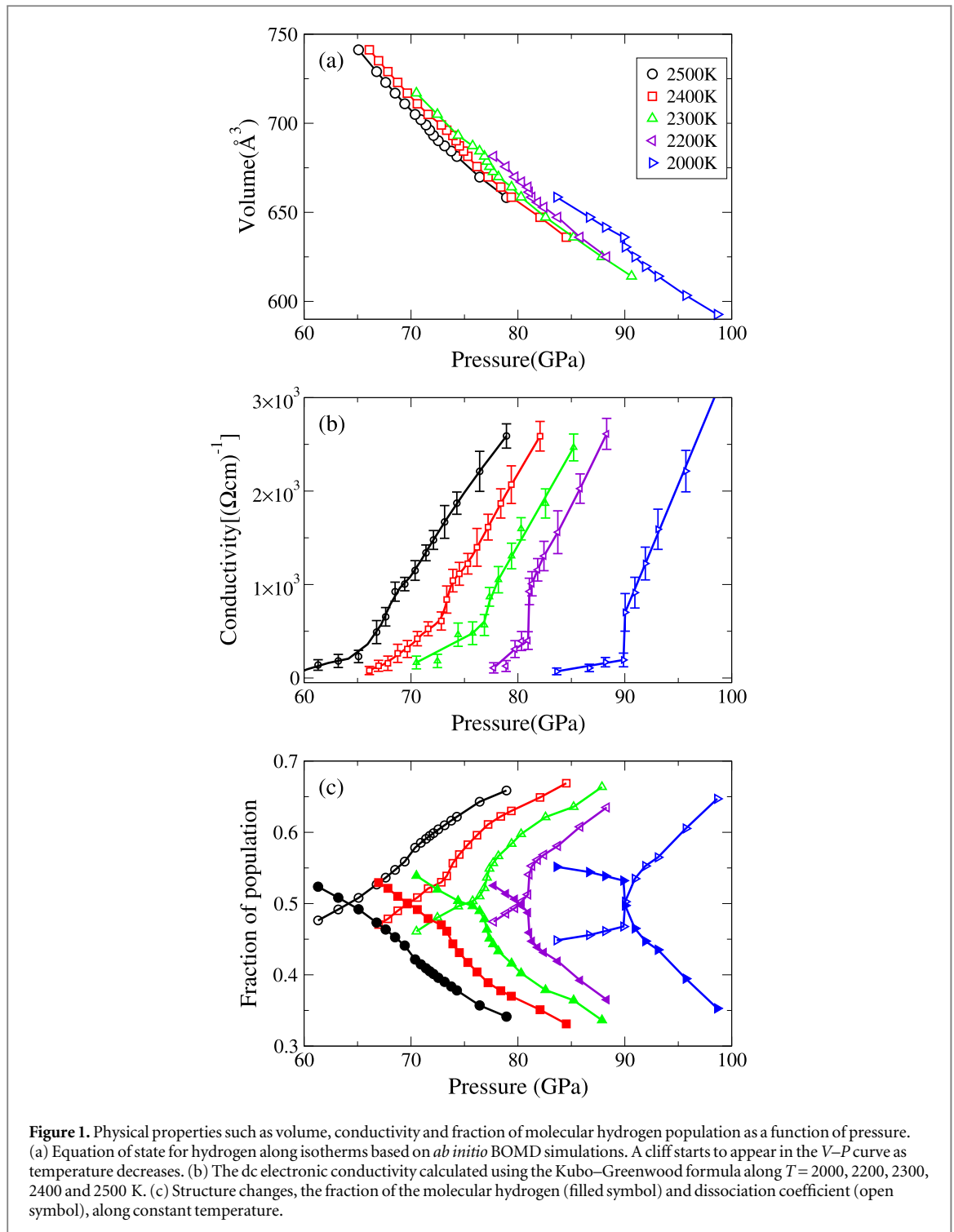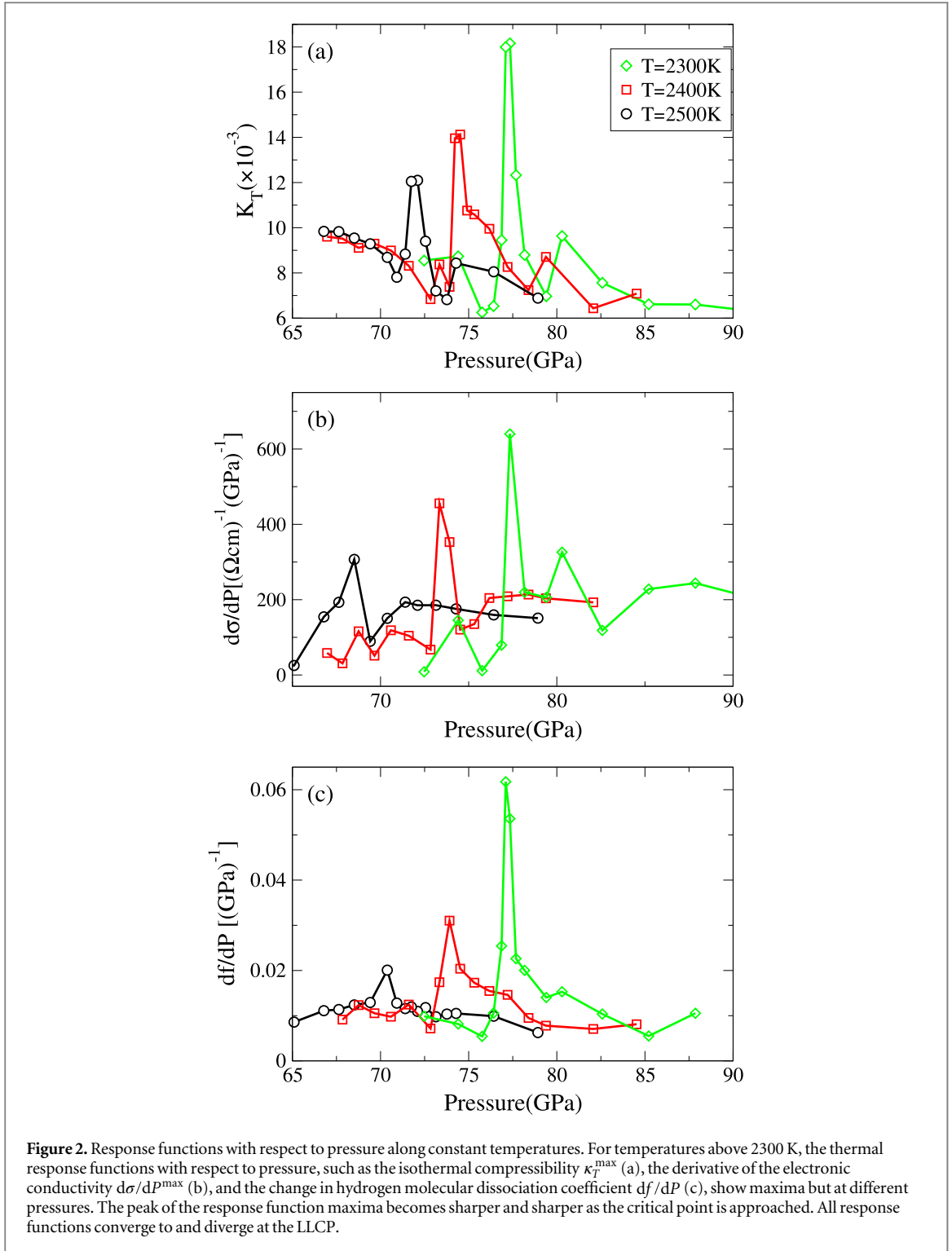
figure 3. As temperature decreases, the loci of different response function maxima asymptotically merge to a single line—the Widom line in the vicinity of the LLCP from supercritical region and terminate at a LLCP located between (2300 K, 77 GPa) and (2200 K, 81 GPa) within resolution, at which all response functions diverge.

The above analysis provides a simple picture for the LLPT in hydrogen under high pressures, which is consistent with [15]. The difference is that we approach the LLCP using supercritical phenomenon from the supercritical region. That is, instead of tracing the LLCP by the terminal point of the first-order LLPT line, we determine the LLCP by investigating the supercritical phenomenon along the Widom line, loci of response functions maxima in the vicinity of the LLCP. This allows us to identify the difference between the insulating-to-metallic and molecular-to-atomic transitions in the supercritical region and numerically locates the critical point. For instance, according to our study, previously reported continuous transitions of hydrogen at high

Figure 2. Response functions with respect to pressure along constant temperatures. For temperatures above 2300 K, the thermal response functions with respect to pressure, such as the isothermal compressibility κ_T^{max} (a), the derivative of the electronic conductivity $d\sigma/dP^{max}$ (b), and the change in hydrogen molecular dissociation coefficient df/dP (c), show maxima but at different pressures. The peak of the response function maxima becomes sharper and sharper as the critical point is approached. All response functions converge to and diverge at the LLCP.

temperatures, insulating-to-metallic and molecular-to-atomic transitions which corresponding to the response of the electric conductivity and molecular dissociation coefficient respectively, are different transitions in the supercritical region. Our results clarify this difference and also find the two transitions are both connected to the LLCP. We point out that this difference gradually disappears as the LLCP is approached, indicating the same origin for the different continuous transitions of hydrogen observed at high temperatures. We note that our results are based on simulations using the PBE exchange-correlation functional for the description of the electronic interactions with the nuclear quantum effects neglected due to the limitation of the computational cost we can afford. Some recent studies using electronic structures generated with other exchange-correlation functionals within DFT or quantum Monte-Carlo method have revealed that a more delicate treatment of the electronic exchange-correlation interactions may lead the transition region to higher pressures [29–31]. We

Figure 3. The *P–T* phase diagram for liquid hydrogen. As shown in the inset, the loci of different response function maxima, $\kappa_T^{\max}$ (open circle), $(d\sigma/dP)^{\max}$ (open square), $(df/dP)^{\max}$ (open diamond), are different. This difference in pressure along each isotherm for two continuous transitions, metal-to-insulator and molecular-to-atomic, becomes smaller and disappears as the liquid–liquid critical point (filled circle) is approached from the supercritical region, at which the peak of the response function maxima also diverge. Thus we can locate the LLCP of hydrogen by tracing the converging of response function extrema from the supercritical region. Below the LLCP, the response functions (e.g., κ_T, $d\sigma/dP$, df/dP) diverge as the first-order LLPT line (filled square) is crossed. We note that melting curves below 200 GPa (brown curve) and above 500 GPa (pink curve) are from [32] and [33]. The LLPT transition line (violet curve) is from [15]. Phase boundaries between different phases (green curve) are from [34].

emphasis that this study is to present an alternative approach which one can employ to investigate the LLPT of hydrogen from the supercritical region at high temperatures and low pressures. For the influence of going beyond PBE and including nuclear quantum effects, we resort the readers to [15, 17, 19, 29–31].

To conclude, we investigate the phase diagram and supercritical phenomenon of hydrogen in the supercritical region of the LLCP. This is important for the interpretation of experimental data performed at high temperatures and low pressures. Firstly, earlier experimental measurements on electric conductivity are performed at ∼3000 K [16, 27, 28]. According to the above picture, this continuous transition is associated with the supercritical phenomenon of the LLCP in the supercritical region of the phase diagram. In contrast, discontinuous transitions at low temperatures and high pressures, e.g., discontinuous insulating-to-metallic transition and molecular dissociation, are due to first-order phase transition below the LLCP in the two phase region. Secondly, the difference between molecular dissociation and insulator-to-metal transition in the continuous transition region indicates that they are rigorously the same only at the LLCP and in the first-order LLPT region. One needs to be aware of their difference when transitions in the supercritical region are studied. Thirdly, we provide a possible approach to locate the LLCP of hydrogen by tracing the loci of the Widom line in the supercritical region. This indicates that the supercritical phenomenon in the vicinity of the LLCP of hydrogen is a rather general feature of second-order phase transition, it is not only true for classical systems with weak interactions but also true for highly condensed system with strong inter-atomic interactions.

Acknowledgments

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