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Response to Comment on "Insulator-metal transition in dense fluid deuterium"

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In their comment Desjarlais, Knudson and Redmer claim that a small temperature drop occurs after isentropic compression of fluid deuterium through the first-order insulator-metal transition. We show that their calculations do not correspond to the experimental thermodynamic path, and that thermodynamic integrations with parameters from first-principles calculations produce results in agreement with our original estimate of the temperature drop.

The recent experiments reported in Celliers *et al.* (*1*) and earlier experiments of Knudson *et al.* (*2*) compressed samples of liquid deuterium to higher than 300 GPa using quasi-isentropic compression methods. Optical reflectance signals from the two experiments show distinct transitions at two different pressures $P_1 \approx 200$ GPa (*1*) and $P_2 \approx 300$ GPa (*2*). According to our interpretation of both experiments, in *(1)* the samples were inertially-confined because of short time scales and the optical reflectance tracked the initial stages of the first-order insulator-metal (IM) transition at pressure P_1; in *(2)* much longer time scales and lateral gradients resulted in turbulent mixing which suppressed the optical reflectance signal until the IM transition was complete, at pressure P_2. Therefore,

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we think the two experiments identify the pressures at start and completion of the IM transition respectively, *i.e.* the pressure extent over which the isentrope passes through the coexistence region. The transformation observed in the experiments spans a pressure change of $\Delta P_{\mathrm{IM}}\approx 95$ GPa and a relative specific volume change of $\Delta V/V_1\approx -0.2$ while conserving entropy $\Delta S\approx 0$. Assuming the temperature is T_1 at the start of the transition the goal is to estimate T_2 at P_2. First, we review the method used by Desjarlais, Knudson and Redmer, then follow with a detailed thermodynamic analysis.

Desjarlais *et al.* use specific heat to estimate T_2/T_1. They provide two evaluations using parameters obtained from *ab initio* models: the specific heat at constant pressure C_P in the metallic fluid (equation 2 or DKR-2), and the specific heat in the coexisting two-phase fluid C_{coex} (equation 3 or DKR-3). The definition of specific heat $C_X = dQ/dT|_X = TdS/dT|_X$ describes the temperature change associated with heat transfer under constraint $\Delta X=0$; note that entropy is not conserved, $\Delta S=\Delta Q/T$. To obtain a temperature drop Desjarlais *et al.* need $\Delta Q < 0$, so they extract the latent heat ($-\Delta H_{\mathrm{IM}}$) from the fluid (*i.e.* cooling) even though $\Delta S=0$ in the experiments. As justification Desjarlais *et al.* state: "Traversal of the phase boundary isothermally ... results in an increase in entropy …"; however, there can be no increase in entropy during isentropic compression, and isothermal traversal cannot occur in the experiments. DKR-2 constrains $\Delta X=\Delta P=0$ while DKR-3 constrains cooling to be along the coexistence line. Using the Maxwell relations we can reduce DKR-3 to equation 4.19 in (*3*), $C_{\mathrm{coex}} = T(dS/dT|_{\mathrm{coex}}) = C_P - T(dV/dT|_P)(dP/dT|_{\mathrm{coex}})$, which gives the specific heat of a substance in two-phase coexistence at constant V, such as liquid water and its vapor in a sealed container, *i.e.* the constraint is $\Delta X=\Delta V=0$. The constraint $\Delta V=0$ causes P to increase as T decreases, like the experiments, but cooling transforms metal to insulator, contrary to the experiments. To recapitulate: Desjarlais *et al.* calculate *cooling* ($\Delta S=-\Delta H_{\mathrm{IM}}/T$), either isobaric ($\Delta P=0$, DKR-2) or isochoric ($\Delta V=0$, DKR-3), in both cases transforming metal to insulator. There is no correspondence to the experiments where isentropic ($\Delta S=0$) compression ($\Delta P_{\mathrm{IM}}\approx 95$ GPa and $\Delta V/V_1\approx -0.2$) transforms insulator to metal.

The compression path, sketched in Fig. 1, follows isentrope S_1^I to the coexistence line at (P_1, T_1), then enters the mixed phase region and follows the coexistence line to (P_2, T_2)

where the transformation is complete; further compression continues along S_2^M. Since the process is isentropic $S_2^M = S_1^I$. Superscripts *I* and *M* refer to the insulating and metallic phases, respectively. Two other isentropes S_2^I and S_1^M intersect the coexistence line at (P_2, T_2) and (P_1, T_1), respectively. At (P_1, T_1) the phase transition can be accomplished by heating at constant *T* and *P* with heat energy ΔQ_1 equal to the latent heat at T_1: $\Delta Q_1 = \Delta H_{\mathrm{IM}}(T_1) = T_1 \Delta S_{\mathrm{IM}}(T_1)$ where $\Delta S_{\mathrm{IM}}(T_1) = S_1^M - S_1^I$; in general ΔS_{IM} is a function of *T*. Since $S_2^M = S_1^I$ it follows that $\Delta S_{\mathrm{IM}}(T_1) = S_1^M - S_2^M$, and $\Delta S_{\mathrm{IM}}(T_2) = S_1^I - S_2^I$.

We can calculate T_2/T_1 along a path comprising a connected sequence of reversible thermodynamic process steps, α, spanning the IM transition and subject to the constraints $\sum_\alpha \Delta S_\alpha = 0$ and $\sum_\alpha \Delta P_\alpha = \Delta P_{\mathrm{IM}}$. One possibility is sketched in Fig. 1, on both the *T*-*P* and *S*-*P* planes: three steps starting with 100% fraction of the insulating phase at (P_1, T_1). We label each step, and its *T* at completion, with the subscripts $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ respectively. Step $\boldsymbol{a}$ is isobaric and isothermal heating by the latent heat $\Delta Q_{\boldsymbol{a}} = \Delta H_{\mathrm{IM}}(T_1) = T_1 \Delta S_{\mathrm{IM}}(T_1)$ to transform from insulator to metal: therefore $\Delta S_{\boldsymbol{a}} = +\Delta S_{\mathrm{IM}}(T_1)$, $\Delta P_{\boldsymbol{a}} = 0$, and $\Delta T_{\boldsymbol{a}} = 0$. Step $\boldsymbol{b}$ is isentropic compression from (P_1, $T_{\boldsymbol{a}}$) to (P_2, $T_{\boldsymbol{b}}$) along S_1^M in the pure metallic phase: $\Delta S_{\boldsymbol{b}} = 0$ and $\Delta P_{\boldsymbol{b}} \approx 95$ GPa. Finally, step $\boldsymbol{c}$ is isobaric cooling (*i.e.* DKR-2) from (P_2, $T_{\boldsymbol{b}}$, S_1^M) to (P_2, $T_{\boldsymbol{c}}$, S_2^M): $\Delta S_{\boldsymbol{c}} = -\Delta S_{\mathrm{IM}}(T_1)$ and $\Delta P_{\boldsymbol{c}} = 0$. By construction $\sum_\alpha \Delta S_\alpha = 0$, $\sum_\alpha \Delta P_\alpha = \Delta P_{\mathrm{IM}}$ and insulator transforms to metal. After step $\boldsymbol{a}$ $T_{\boldsymbol{a}} = T_1$ because $\Delta T_{\boldsymbol{a}} = 0$; therefore, $T_2/T_1 = (T_{\boldsymbol{b}}/T_{\boldsymbol{a}})\,(T_{\boldsymbol{c}}/T_{\boldsymbol{b}})$. The DKR-2 calculation provides $T_{\boldsymbol{c}}/T_{\boldsymbol{b}} \approx 0.83$ (step $\boldsymbol{c}$). The remaining term, $T_{\boldsymbol{b}}/T_{\boldsymbol{a}}$, can be determined from the slope of the isentrope in the pure metallic phase. From basic thermodynamic principles $T\, dP/dT|_S = B_S/\gamma$ where B_S is the isentropic bulk modulus and γ is the Grüneisen parameter. Integration along the isentrope from (P_1, T_a) to (P_2, T_b) leads to $\int_{T_{\boldsymbol{a}}}^{T_{\boldsymbol{b}}} dT/T = \int_{P_1}^{P_2} dP\, \gamma/B_S$, or $T_{\boldsymbol{b}}/T_{\boldsymbol{a}} = \exp\left[\int_{P_1}^{P_2} dP\, \gamma/B_S\right]$. The slope is negative because $\gamma < 0$ (as noted in Desjarlais *et al.*); therefore $T_{\boldsymbol{b}} < T_{\boldsymbol{a}}$. We estimate $\gamma \approx -1.2$ by examining the isentropes plotted in Fig. 1 of *(2)*; note that the value $\gamma = -2.3$ from Desjarlais *et al.* does not apply because it was evaluated within the coexistence region, not the pure metallic phase. Substituting $B_S \approx 525$ GPa (interpolated from Pierleoni *et al.* (*4*) supplementary Table V near 240 GPa, midway along the isentrope between P_1, $T_{\boldsymbol{a}}$ and P_2, $T_{\boldsymbol{b}}$) and $\gamma \approx -1.2$ we find $T_{\boldsymbol{b}}/T_{\boldsymbol{a}} \approx 0.80$, thus $T_2/T_1 = (T_{\boldsymbol{b}}/T_{\boldsymbol{a}})\,(T_{\boldsymbol{c}}/T_{\boldsymbol{b}}) \approx 0.80 \times 0.83 \approx 0.66$. The path chosen for the calculation is not unique. A similar calculation on the insulating side of

the transition is: **a***, isobaric cooling from (P_1, T_1) to reduce the entropy by $-\Delta S_{\mathrm{IM}}(T_2)$; **b***, isentropic compression along S_2^I from P_1 to (P_2, T_2, S_2^I); and **c***, isothermal and isobaric heating by $+\Delta H_{\mathrm{IM}}(T_2)=T_2\Delta S_{\mathrm{IM}}(T_2)$ to transform from insulator to metal, reaching (P_2, T_2, S_2^M).

T_2/T_1 can also be calculated by direct integration of the Clausius-Clapeyron equation along the coexistence line: $\int_{T_1}^{T_2} dT/T = \int_{P_1}^{P_2} dP\ \Delta V_{\mathrm{IM}}(P)/\Delta H_{\mathrm{IM}}(P)$, where the integration starts at (T_1, P_1) and terminates at (T_2, P_2). Here $\Delta V_{\mathrm{IM}}(P)$ and $\Delta H_{\mathrm{IM}}(P)$ are the volume change and latent heat as a function of pressure along the coexistence line. From this equation $T_2/T_1 = \exp\left[\int_{P_1}^{P_2} dP\ \Delta V_{\mathrm{IM}}(P)/\Delta H_{\mathrm{IM}}(P)\right]$. Using estimates for $\Delta H_{\mathrm{IM}}\approx 2.62$ kJ/g from Pierleoni *et al.* (*4*), a 3% volume discontinuity $\Delta V_{\mathrm{IM}}\approx -0.015$ cm^3/g estimated from several studies (*4–7*), and from the experiments (P_2 -P_1)≈95 GPa we find $T_2/T_1 \approx 0.58$. The original estimate in Celliers *et al.* (*1*), based on a finite difference evaluation of the Clausius-Clapeyron equation, resulted in a scaling factor for $\Delta T = T_2 - T_1 = f\,T_1$, where f=– 0.49±0.16; therefore $T_2/T_1 = f + 1$=0.51±0.16. Our study *(1)* also accounted for cooling from the aluminum piston in *(2)* which, combined with long time scales, turbulent mixing and convective heat exchange, might account for a large temperature drop; however, quantitative calculations found a small effect (≈100 K) because the heat capacity of the aluminum piston is much lower than that of the deuterium fluid. Thus, the experimental path is isentropic to a good approximation, and to simplify the discussion in this response we considered purely isentropic processes. The two new estimates given here agree within the uncertainty stated in (*1*).

To summarize: thermodynamic path integration is in reasonable agreement with Clausius-Clapeyron integration; all estimates are within the uncertainty range quoted in (*1*); and finally, anomalous specific heat is not required to explain the temperature drop, contrary to the conclusion of Desjarlais *et al.* Key to these calculations are accurate values for γ, B_S and C_P near the IM transition, also $\Delta V_{\mathrm{IM}}(P)$ and $\Delta H_{\mathrm{IM}}(P)$.

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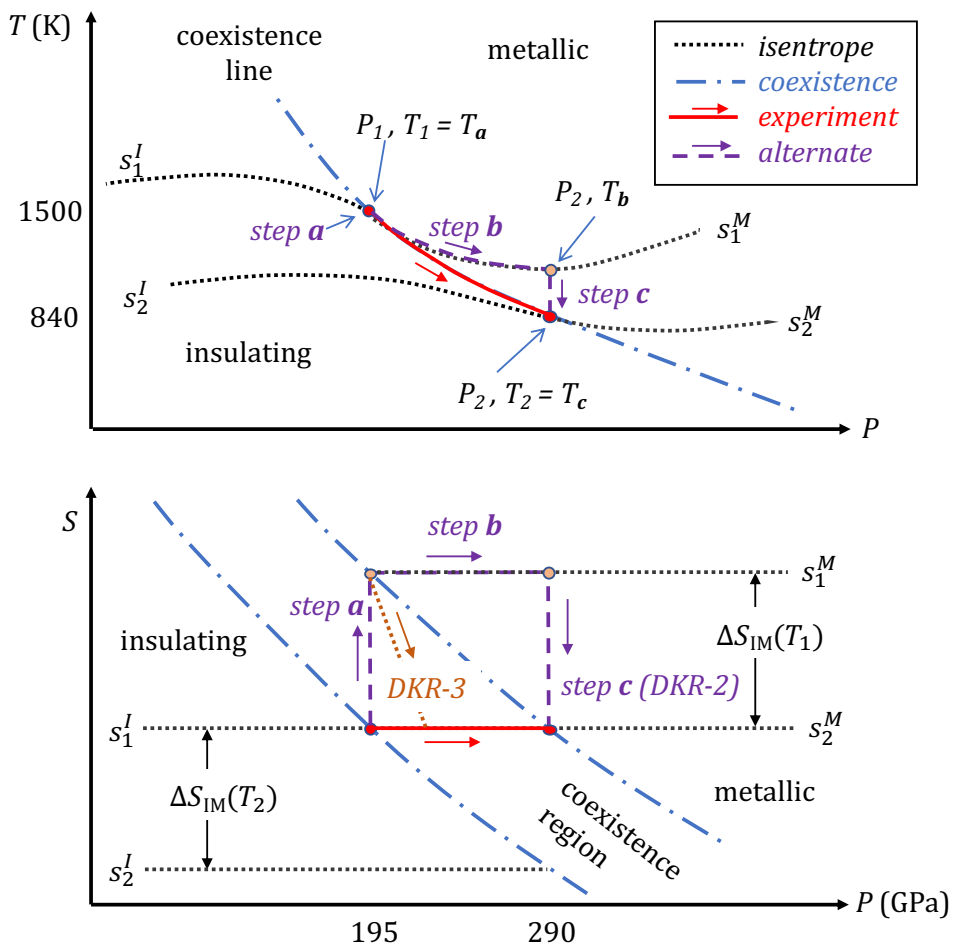

Fig. 1. Upper (lower) frame shows thermodynamic paths on the *T*-*P* (*S*-*P*) plane, both frames share the same *P* scale. The experimental compression path (red solid line segments) enters the mixed phase coexistence region at (P_1, T_1, S_1^I) and follows the coexistence line at equilibrium (blue chain-dashed curve on upper frame) until the transformation is complete at (P_2, T_2, $S_2^M = S_1^I$). For *T* calculations an alternate path (purple dashed curves) is: step ***a***, isobaric and isothermal heating by $+\Delta H_{IM}(T_1)=T_1\Delta S_{IM}(T_1)$ to transform from insulator (P_1, T_1, S_1^I) to metal (P_1, T_1, S_1^M); step ***b***, isentropic compression along S_1^M from (P_1, T_a=T_1, S_1^M) to (P_2, T_b, S_1^M); and, step ***c***, isobaric cooling from T_b to T_c to reach (P_2, T_c=T_2, $S_2^M = S_1^I$). Step ***c*** corresponds to Desjarlais *et al.* equation 2 (DKR-2). Desjarlais *et al.* equation 3 (DKR-3) follows an isochore in the coexistence region and drives the transition from metal to insulator, contrary to the experiments (see text). Neither DKR-2 nor DKR-3 corresponds to the experimental path.