Response to Comment on "Third density and acoustic virial coefficients of helium isotopologues from *ab initio* calculations" [J. Chem. Phys. 160, 244305 (2024)]

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In a recent paper,[1] we presented first-principles calculations of the third density and acoustic virial coefficients for ^{3}He and ^{4}He from state-of-the-art pair and three-body potentials. The uncertainties of our calculations, based on uncertainties of the potentials, were smaller than any available from experiment.

In the preceding Comment,[2] Tada correctly points out that we failed to include comparisons with experimental data for ^{3}He despite the fact that a few sources of data exist. In fact, we had previously been aware of some data for ^{3}He, and even cited them in earlier work,[3] so we have no excuse for our erroneous statement in Ref. 1 that such data were lacking.

Tada shows good agreement between our calculations and data for the third acoustic virial coefficient. For the third density virial coefficient $C(T)$, three sources are plotted for ^{3}He, all of which deviate from our calculations in the positive direction. The deviations are mostly larger than the error bars on the experimental values, although the reported error bars appear to be statistics from a fit and not a complete uncertainty budget, meaning that they likely underestimate the uncertainty. Two of the sources are older work from the USSR,[4,5] while the third is values derived by Tada[6] from analysis of the volumetric data of Bogoyavlenskii *et al.*[7] While we agree that new, reliable measurements on ^{3}He at low temperatures would be desirable, we explain below why we believe our calculated results are correct.

I. DATA SOURCES FOR ^{3}HE

The three sources for $C(T)$ plotted in the Comment are not all independent. They were all based on data measured at the Physicotechnical Institute of the Academy of Sciences of the Ukrainian SSR. It is instructive to review the different measurements and publications.

In 1974, Karnus and Rudenko[8] published density data for ^{3}He at temperatures from 14–60 K at pressures from approximately 0.4 MPa to 11 MPa. In 1976, Karnus[4] analyzed these data and derived values of C that were stated to have a standard uncertainty of 50 cm^6 mol^{-2}.

A different apparatus, based on dielectric resonance, was designed for measurements below 14 K. In 1978, Bogoyavlenskii *et al.*[7] reported densities for ^{3}He on 11 isotherms from 3.33–13 K. The pressure range began below 0.07 MPa for each isotherm and typically extended to near 10 MPa. No virial coefficients were reported.

The 1988 paper of Karnatsevich *et al.*[5] requires careful reading. They used the same apparatus as Bogoyavlenskii *et al.*,[7] but with greater attention to measuring low pressures, to accuracy of the resonance measurements, and to temperature calibration. They took data between approximately 0.02 MPa and 0.3 MPa along five isotherms. They derived second and third virial coefficients, but because the upper pressure limit was only 0.3 MPa, the few values of C from these isotherms had large uncertainties.

The important point for this Response (which we only recently noticed) is that most values of C reported in the paper of Karnatsevich *et al.*[5] did *not* come from their 1988 measurements. They derived most of their values of C by analyzing the 1978 density data of Bogoyavlenskii *et al.*,[7] with temperatures corrected to reflect their improved calibration. As a result, the 1988 Karnatsevich values[5] and the 2021 Tada values[6] are essentially duplicates, since they are both based on the density data of Bogoyavlenskii *et al.*[7] Their agreement is therefore expected.

In Fig. 1, we plot data for $C(T)$ of ^{3}He, separating the values (with large error bars) that Karnatsevich *et al.*[5] derived from their 1988 measurements from those they derived from the 1978 data of Bogoyavlenskii *et al.* We also show two sources not mentioned in the Comment. Fellmuth and Schuster[9] presented an equation for $C(T)$ from 1.5–3.8 K, based on unpublished work by Steur who fitted density data from Keller[10] constrained by accurate theoretical values of the second virial coefficient B. The equation is fairly consistent with our results. Gaiser and Fellmuth[11] measured ^{3}He at 2.466 K and 3.232 K by dielectric-constant gas thermometry (DCGT). Preliminary values of C derived from these measurements were cited in Ref. 3, but very recently Gaiser has reanalyzed the data[12] with the aid of accurate *ab initio* dielectric virial coefficients for ^{3}He.[13,14] As seen in Fig. 1, these two points are in excellent agreement with our calculations.

We also note (as mentioned in the Comment) the agreement between our calculations and the third acoustic virial coefficients of Grimsrud and Werntz.[15] Grimsrud and Werntz also measured ^{4}He, and previous work[16] showed that calculated

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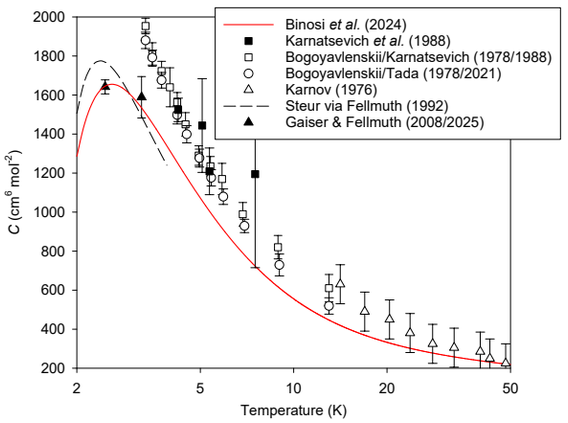

FIG. 1. Comparison of calculated $C(T)$ for ^{3}He with experimental values at cryogenic temperatures. Error bars on experimental points represent expanded uncertainties with coverage factor $k = 2$.

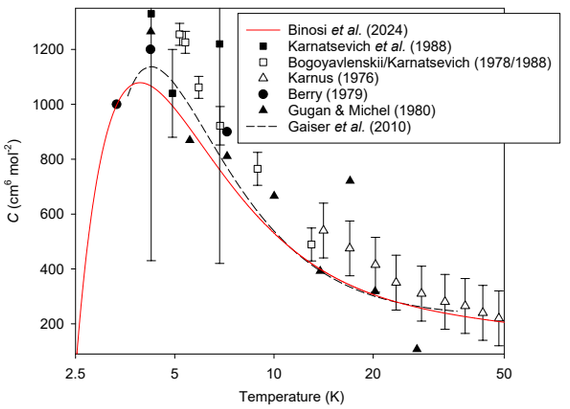

FIG. 2. Comparison of calculated $C(T)$ for ^{4}He with experimental values at cryogenic temperatures. Error bars on experimental points represent expanded uncertainties with coverage factor $k = 2$ and are not shown for Berry[19] or for Gugan and Michel.[20]

results agree both with those data and with another source of third acoustic virial coefficients for ^{4}He at low temperatures.[17] Because the acoustic virial coefficient depends on $C(T)$, the second virial coefficient $B(T)$, and their first two temperature derivatives,[18] that provides indirect validation of calculated $C(T)$.

II. COMPARISON WITH ^{4}HE

Additional evidence that the three experimental sources for $C(T)$ mentioned in the Comment[2] (at most two of which are independent) that disagree with our calculations are probably inaccurate comes from examining results from the same sources for ^{4}He, where additional data exist. Experimental values of C for ^{4}He at cryogenic temperatures are plotted in Fig. 2. This is similar to Fig. 10 in Ref. 1, but we have omitted one older, scattered data set and distinguished between the points that Karnatsevich *et al.*[5] derived from their 1988 measurements and those they derived from the data of Bogoyavlenskii *et al.*[7] For clarity, we omitted error bars from the points of Berry[19] and of Gugan and Michel;[20] they are on the order of several hundred cm^6 mol^{-2}, which makes them consistent with our results within those large uncertainties.

Figures 1 and 2 show that very similar deviations from theory exist for both isotopes for the data of Karnus[4] and for data based on the densities of Bogoyavlenskii *et al.*[7] This eliminates the possibility of an error specfic to our ^{3}He calculations (e.g., in treatment of exchange for fermions). Either our calculations for both isotopes are in error or the two experimental studies[7,8] have systematic errors.

Fortunately, for ^{4}He there are additional data to validate our calculations. Other sources shown as points on Fig. 2 generally agree with our calculations, but their uncertainties are too large to be very useful. The most important experimental results on Fig. 2 are those of Gaiser *et al.*[21] These values were fitted to high-accuracy DCGT data from 3.7–36 K, using much of the same apparatus that was used to measure the Boltzmann constant to a relative standard uncertainty near 2×10^{-6}.[22] While the uncertainty of $C(T)$ from Ref. 21 is not completely clear, an earlier paper from the same group[23] suggests that the standard uncertainty of C from DCGT is on the order of 10 cm^6 mol^{-2} above 6 K, rising to 100 cm^6 mol^{-2} as the temperature approaches 3 K. This means that the results of Ref. 21, shown as the dashed curve in Fig. 2, are consistent with our calculated $C(T)$ for ^{4}He. We consider these high-quality DCGT results to be strong evidence that our calculations are correct and the two older data sources have systematic errors.

Additional validation of our results comes from the excellent agreement between calculated $C(T)$ for ^{4}He near room temperature and the best experimental sources, as shown in Ref. 1. However, this is weak confirmation; quantum effects are small at those temperatures so an error in the quantum part of the calculations might not be apparent.

III. CONCLUSIONS

Similar discrepancies exist between some experimental sources of $C(T)$ at low temperatures and our calculated values for both ^{3}He (as pointed out by Tada[2]) and ^{4}He. The agreement of calculated results for both ^{3}He and ^{4}He with values from state-of-the-art DCGT experiments (along with agreement with third acoustic virial coefficients) leads us to believe that the problem lies with the older experimental data sources. The $C(T)$ from Karnus[4] agree with our results above 20 K, but disagree in the range 14–20 K. Values derived from the densities of Bogoyavlenskii *et al.*,[7] both by Karnetsevich *et al.*[5] and (for ^{3}He) by Tada,[6] seem to be systematically high.

We have no hypothesis for the disagreement with the results of Karnus,[4] but we note a problem with the densities of Bogoyavlenskii *et al.*[7] While the paper reported density,

they actually measured the static dielectric constant, which was converted to density by a formula for the polarizability given in 1970 by Kerr and Sherman.[24] Much more accurate information now exists from theory for the polarizability of a helium atom[25] and for the effect of density on the polarization (second[13] and third[14] dielectric virial coefficients). Based on this improved dielectric information, the densities reported by Bogoyavlenskii *et al.*[7] would have been too high by amounts on the order of 0.1%. This would surely distort derived virial coefficients.

We agree with the Comment that new experimental data for $C(T)$ of ^{3}He at cryogenic temperatures are desirable; the two DCGT data from Gaiser and Fellmuth[11,12] provide confirmation, but independent verification is always good. It is unlikely that experiments could match the uncertainty of the calculations of Ref. 1, but agreement within mutual uncertainties would increase confidence in the calculations. The expense of ^{3}He is an obstacle, but some institutes have existing stocks of ^{3}He that might be used.

We would also welcome independent verification of our calculations. A recent review on calculated gas properties in metrology noted that independent validation of potential-energy surfaces and of the quantum calculation of virial coefficients is lacking in many cases.[26] Mistakes can happen in calculations as well as in experiments; more validation is needed, analogous to the replication that is desirable for experimental data.

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