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Scaling relations for two-component charged systems: Application to metallic hydrogen

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We derive exact scaling relations for the energy and pair-correlation functions of a neutral two-component system of charged nonrelativistic particles in its ground state. These are obtained under general conditions through the use of the virial theorem, and the use of the Hellmann-Feynman theorem with respect to masses and charges, and they are independent of symmetry. For a dense system of charged fermions of disparate masses, where Born-Oppenheimer separation is valid, these results are used to obtain the ground-state energy by scaling from known electron-gas results and evaluating terms from cross interactions by response and effective-mass theory. The results, which require very little numerical work, agree well with the quantum Monte Çarlo simulations for metallic hydrogen.

I. INTRODUCTION

A dense assembly of ions with unit charge, and a compensating system of electrons might, in one sense, be considered as a relatively simple form of matter in the condensed state. However, if the ion involved lacks an internal electronic structure of its own, as in the example of protons, and at the same time the ion is itself relatively light, the resulting system at sufficiently high density, in this case metallic hydrogen, can display significant quantal behavior in both electrons and ions. Depending on the nature of the ground and nearby states, i.e., whether these are crystalline or liquid, the overall system can yield a range of subtle orderings that actually render its description as far from simple. Yet in spite of this complexity, the fundamental Hamiltonian *is* simple and has a high degree of symmetry. So far as the interactions are concerned, they are entirely Coulombic, there is no spin dependence, and on a scale relevant to condensed-matter physics all particles are point particles. Given this, questions can be asked about the most general statements that can be made about both the thermodynamic and correlation or structure functions of the system as a function of density irrespective of the details of the orderings noted earlier, and resulting from only a global specification of the states (e.g., that they possess homologous structures). Because the Hamiltonian admits of only a single length scale, essentially the inverse cube root of the density, it provides some important scaling properties, as we shall see, which can be used to give at least partial answers to these questions. The primary purpose of this paper is to exploit this scaling behavior to arrive at conclusions about the energy of the system as a function of density.

This matter is taken up in Sec. II, where a scaling property for the total energy is proved from general principles (use of the virial and Hellmann-Feynman theorems). This scaling rule is then combined with the Vosko-Wilk-Nusair approximate expression for the energy of an electron gas to deduce an accurate approximation for the mass dependence of the energy of one-component charged fermions in the paramagnetic phase, but immersed in a uniform neutralizing background. This expression is then used to establish the Madelung energy for a proton system and to estimate the zero-point energy. As an example of a very general statement valid for a Coulomb system, a generalization of the expression for the energy of particles of arbitrary mass and charge, based on a second independent scaling relation, is given in Appendix A. Additional general scaling properties are derived in Appendix B for the partial static structure factors and pair-distribution functions of the two-component system, and their consistency with the thermodynamic scaling relations is established. The results obtained in Sec. II are used in the description of a two-component system in Sec. III, where the problem is now split into three parts, namely two separate one-component problems and a coupling between them. The two one-component parts are accurately described by the results of Sec. II, while the third is treated by the Hellmann-Feynman theorem with respect to an appropriately introduced coupling constant in the two-component Hamiltonian. By limiting ourselves within the usual Born-Oppenheimer approximation and proceeding first within the context of linear-response theory, we propose a simple approximate model that is also shown to be consistent with the scaling constraints. The solution of the resulting problem requires a specific form for the proton-proton partial structure factor $S_{pp}(q)$ as well as for the static local field $G(q)$ describing the response of the electron gas to the screened field of the protons. In Sec. IV we give arguments for a particular choice of $S_{pp}(q)$; two separate models for $G(q)$ are also used, as will be seen. The results, discussed in Sec. V, show excellent agreement with the Monte-Carlo-simulation results[1] for metallic hydrogen up to $r_s \sim 1.4$. It is also shown there how we can obtain the Monte Carlo results for the entire available range of r_s from 1 to 2, by using an effective-mass approach (which approximates nonlinear response) in the determination of the electron-proton coupling term. The scaling relations of Sec. II are once again used in an independent way in this effective mass approach, proving that they are of considerable importance for the problem. A discussion of the model proton-proton structure factor is included in Appendix D, in the context of a rigorous variational argument that actually gives an *upper bound* to the ground-state energy of the two-component system.

The simple model for metallic hydrogen proposed here is not sufficiently accurate to distinguish between a solid and a liquid proton phase, the energy difference being exceedingly small (of the order of millirydbergs per particle). Rather it exploits the smallness of this energy difference to provide a very simple way of deriving the quantum Monte-Carlo-simulation results for metallic hydrogen starting from very general principles and from the known Monte Carlo results for the electron-gas problem.

II. GENERAL RELATIONS

Let us consider a neutral system of N positive charges (Ze) with mass m_p and ZN negative charges $(-e)$ with mass m_e (considered as point particles) in volume V. Examples might be hydrogen[1-9] or muonium, or electrons and holes.[10] We will work with protons from now on $(Z=1)$, although a generalization for arbitrary charges Z_1 and Z_2 is also given in Appendix A. Omitting relativistic corrections, the Hamiltonian of this system is

$$H=\sum_{i=1}^{N}\frac{p_{i,e}^2}{2m_e}+\sum_{i=1}^{N}\frac{p_{i,p}^2}{2m_p}+\tfrac{1}{2}\sum_i\sum_{j\neq i}\frac{e^2}{|\mathbf{r}_{i,e}-\mathbf{r}_{j,e}|}+\tfrac{1}{2}\sum_i\sum_{j\neq i}\frac{e^2}{|\mathbf{r}_{i,p}-\mathbf{r}_{j,p}|}-\sum_i\sum_j\frac{e^2}{|\mathbf{r}_{i,e}-\mathbf{r}_{j,p}|}\ . \tag{1}$$

We immediately rescale all variables using

$$V=N\tfrac{4}{3}\pi r_0^3,\quad r_s=\frac{r_0}{a},\quad a=\frac{\hbar^2}{\overline{m}e^2}=\frac{M}{m_p}a_0\ ,$$

$$M=m_e+m_p,\quad \overline{m}=\frac{m_e m_p}{M}\ ,$$

and

$$V=\overline{V}r_0^3,\quad \mathbf{r}_e=r_0\overline{\mathbf{r}}_e,\quad \mathbf{r}_p=r_0\overline{\mathbf{r}}_p\ ,$$

$$\mathbf{p}_e=\hbar\overline{\mathbf{p}}_e/r_0,\quad \mathbf{p}_p=\hbar\overline{\mathbf{p}}_p/r_0\ .$$

Equation (1) then reads

$$H=\frac{e^2}{2a}\frac{1}{r_s^2}\left[\frac{m_p}{M}\sum_{i=1}^{N}\overline{p}_{i,e}^{\,2}+\frac{m_e}{M}\sum_{i=1}^{N}\overline{p}_{i,p}^{\,2}+r_s\sum_i\sum_{j\neq i}\frac{1}{|\overline{\mathbf{r}}_{i,e}-\overline{\mathbf{r}}_{j,e}|}+r_s\sum_i\sum_{j\neq i}\frac{1}{|\overline{\mathbf{r}}_{i,p}-\overline{\mathbf{r}}_{j,p}|}-2r_s\sum_i\sum_j\frac{1}{|\overline{\mathbf{r}}_{i,e}-\overline{\mathbf{r}}_{j,p}|}\right]\equiv T_e+T_p+U\ , \tag{2}$$

where T_e and T_p are electron and proton kinetic energies, and U is the sum of all interactions. We now apply the Hellmann-Feynman theorem (HFT) with respect to r_s, namely

$$\frac{\partial\langle\Psi|H|\Psi\rangle}{\partial r_s}=\left\langle\Psi\left|\frac{\partial H}{\partial r_s}\right|\Psi\right\rangle \tag{3}$$

(where[11] $H|\Psi\rangle=E|\Psi\rangle$), and then use the definition of pressure to obtain for the ground state,

$$p=-\left[\frac{\partial\langle H\rangle}{\partial V}\right]_N=-\frac{r_s}{3V}\left[\left\langle\frac{\partial H}{\partial r_s}\right\rangle\right]_N=-\frac{r_s}{3V}\left[-\frac{2\langle T\rangle}{r_s}-\frac{\langle U\rangle}{r_s}\right]\ , \tag{4}$$

where we have written $\langle T\rangle=\langle T_e\rangle+\langle T_p\rangle$. It follows that

$$3pV=2\langle T\rangle+\langle U\rangle\ , \tag{5}$$

which is simply the virial theorem (VT).[12] Another consequence of (2) that we will later use is a pair of exact relations connecting the kinetic or potential energy to the total energy of a general Coulombic system [see Eqs. (48)].

On the other hand, if we apply the HFT to (1) with respect to each mass independently we obtain

$$\frac{\partial\langle H\rangle}{\partial m_e}=-\frac{\langle T_e\rangle}{m_e}$$

and

$$\frac{\partial\langle H\rangle}{\partial m_p}=-\frac{\langle T_p\rangle}{m_p}\ , \tag{6}$$

so that

$$\langle T\rangle=-m_e\frac{\partial\langle H\rangle}{\partial m_e}-m_p\frac{\partial\langle H\rangle}{\partial m_p}\ . \tag{7}$$

The combination of (4) and (7) with $\langle H\rangle=\langle T\rangle+\langle U\rangle$ now yields

$$r_s\frac{\partial E}{\partial r_s}-m_e\frac{\partial E}{\partial m_e}-m_p\frac{\partial E}{\partial m_p}=-E(r_s,m_e,m_p)\ . \tag{8}$$

This is an exact partial differential equation for the full quantum-mechanical internal energy $(E\equiv\langle H\rangle)$ of particles with masses m_e and m_p. The general solution of (8), a linear first-order partial differential equation, is easily found to possess the scaling form

$$\frac{E}{N}=\frac{f(m_e r_s;m_p r_s)}{r_s}\ , \tag{9}$$

which is also therefore an exact property of the energy of the two-component Coulomb system valid for all states. [In Appendix A we also give the dependence of the energy on the charges of the particles; see Eq. (A8).]

Application of the same ideas to the standard one-component Coulomb system of point particles in a rigid uniform compensating background of opposite sign yields the partial differential equation

$$r_s\frac{\partial E}{\partial r_s}-m\frac{\partial E}{\partial m}=-E(r_s,m)\ , \tag{10}$$

with the general solution being in the form

$$\frac{E}{N}=\frac{g(mr_s)}{r_s}\ . \tag{11}$$

[Again for the corresponding dependence of the energy on the charge of the particles, see Eq. (A6).]

In addition to the very general expressions (9) [and (A8)] for the ground-state energy of the two-component system, we also derive in Appendix B the corresponding exact scaling relations for the static partial structure factors and pair distribution functions for the ground state of a general two-component Coulomb system [see Eqs. (B14), (B15), and (B16)].

We now show that these general scaling properties can be used to derive nontrivial results for the combined system providing this is restricted to possess a homologous structure and to undergo no condensation[13] during the change of the parameters. We begin by assuming that the approximate solution for the electron gas immersed in a uniform and nonresponding background[14–18] is known, and in fact can be described by the Padé-approximants correlation-energy expression proposed by Vosko, Wilk, and Nusair[17] (VWN), which is actually very accurate in describing the Monte Carlo results[18] for the paramagnetic phase of the electron liquid over a substantial range of r_s values. Given this form we can now find the corresponding expression for a continuous phase of a proton system immersed in a negative background by imposing condition (11). The result is a unique expression for the total energy per particle (for particles of arbitrary mass m) that satisfies (11) but at the same time tends to the VWN expression for $m\rightarrow m_e$, namely

$$\begin{aligned}\frac{E}{N}(r_s,m)=\frac{A}{x}\Bigg\{&\ln\left[\frac{r_s}{r_s+bx^{1/2}r_s^{1/2}+cx}\right]+\frac{2b}{Q}\tan^{-1}\left[\frac{Qx^{1/2}}{2r_s^{1/2}+bx^{1/2}}\right]\\&-\left[\frac{bx_0}{x_0^2+bx_0+c}\right]\left[\ln\left[\frac{(r_s^{1/2}-x_0x^{1/2})^2}{r_s+bx^{1/2}r_s^{1/2}+cx}\right]+\frac{2(b+2x_0)}{Q}\tan^{-1}\left[\frac{Qx^{1/2}}{2r_s^{1/2}+bx^{1/2}}\right]\right]\Bigg\}\\&+\frac{3}{5}\left[\frac{9\pi}{4}\right]^{2/3}\frac{x}{r_s^2}-\frac{3}{2\pi}\left[\frac{9\pi}{4}\right]^{1/3}\frac{1}{r_s}\ \text{Ry}\end{aligned} \tag{12}$$

where $x=m_e/m$ and the constants have the values $A=0.062\,181\,4$, $b=3.727\,44$, $c=12.9352$, $Q=(4c-b^2)^{1/2}$, and $x_0=-0.104\,98$.

Expression (12) gives the dependence of the energy on the mass m of the positive point unit charge. [See also Eq. (A7) for the dependence on the magnitude of the charge.] The energy for the proton system in a negative background is obtained from the choice $x=1/1836.15$. We plot this energy in Figs. 1 and 2 (curve 2). It has a minimum at very high densities (around $r_s\simeq 0.002$), which is not meaningful since at such densities the system is already relativistic. The energy is monotonically increasing with r_s beyond this point (the physically interesting range is $r_s\sim 1$). In the case of infinitely massive particles, expression (12) has a limit which, within the Padé-approximants derivation of (12) is exact, namely

$$\lim_{m\rightarrow\infty}\frac{E}{N}=\frac{-1.744\,991}{r_s}\ \text{Ry}\ , \tag{13}$$

which can be interpreted as the result for a peculiar limiting case, namely as the quantum-mechanical Madelung energy for particles of infinite mass in an assumed-continuous phase, where account is taken to a very good approximation for both "exchange" (which is present because of the assumed continuity of the phase) and also correlation effects as they are manifested in the structure. For large but finite masses (12) also accounts for zero-

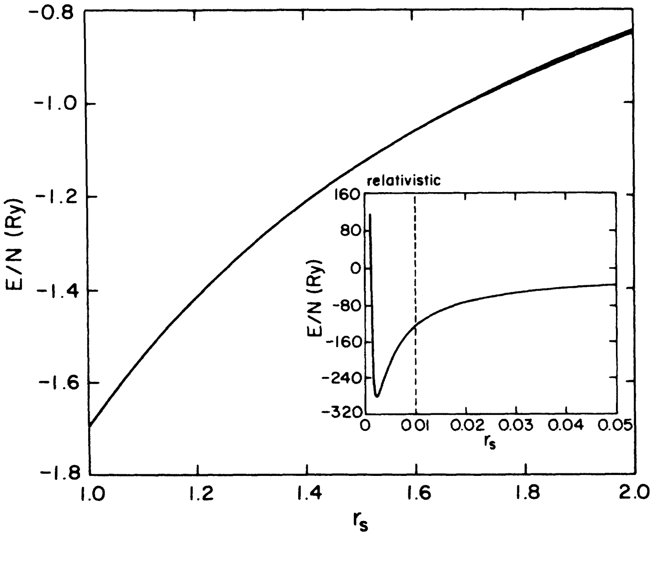

FIG. 1. Comparison of the proton-gas energy (per particle) with the curve $E=-1.70/r_s$ Ry, which describes the proton Madelung energy quite closely in the region $1\le r_s<1.5$. In the inset we show the energy per proton gas in a negative uniform background at very high densities. The minimum has no significance since at the corresponding densities the system becomes relativistic.

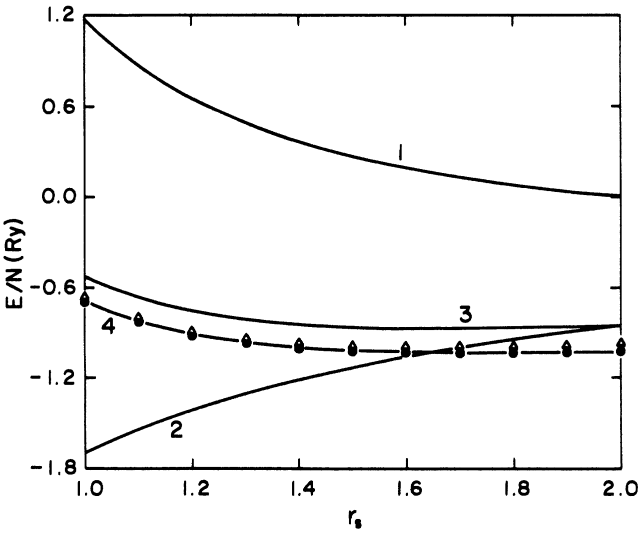

FIG. 2. Energy per particle for an electron gas in a positive background (curve 1), for a proton gas in a negative background (curve 2), curve 3 = curve 1 + curve 2, curve 4 = energy per atom for hydrogen [actual Monte Carlo results (Ref. 1)], and filled circles denote final results of the present work. We also give (triangles) upper bounds for the total energy corresponding to particles of infinite mass (see variational argument in Appendix D).

point-motion effects: Thus by using the actual protonic mass one finds (Fig. 1) that E/N is, to quite high precision,

$$\frac{E}{N} \simeq -\frac{1.70}{r_s}\ \text{Ry} \tag{14}$$

in the region $1 \le r_s < 1.5$, an approximation that will be used in Sec. IV for a starting estimate of the correlations present in the system.

These are important results that we will use later, but we note first, that (13) and (14) are already both close to the ion-sphere result $-9/5r_s$ Ry for the standard Madelung energy of massive point particles in a uniform background. Second, we can easily show that (12) has an expansion around $m = \infty$ of the form

$$\frac{E}{N} = \frac{A}{r_s} + \frac{B}{m^{1/2} r_s^{3/2}} + O\left[\frac{1}{m r_s^2}\right] \text{Ry} ,$$

where $A = -1.744\,991$ [see (13)] and $B = 2.060\,89 m_e^{1/2}$. Again this is close to a known limit, namely the expansion of the energy for a proton Wigner crystal[19] which can be found by applying the exact form (11) to perturbation-theory results[20] for the electron crystal, the result being

$$\frac{-1.791\,86}{r_s} + \frac{2.65 m_e^{1/2}}{r_s^{3/2} m^{1/2}} + O\left[\frac{1}{m r_s^2}\right] \text{Ry} .$$

As a consequence of this result and the fact that m_p/m_e is large we can show, using the exact Coulombic virial theorem (5) [or equivalently by using Eqs. (48), which are also exact], that

$$\frac{\langle T \rangle}{N} = \frac{1}{2} \frac{B}{m^{1/2} r_s^{3/2}} + \cdots \text{Ry}$$

and

$$\frac{\langle U \rangle}{N} = \frac{A}{r_s} + \frac{1}{2} \frac{B}{m^{1/2} r_s^{3/2}} + \cdots \text{Ry} .$$

Therefore for this continuous phase we have the result

$$\begin{aligned} T(m = m_p) &\simeq U(m = m_p) - E(m \to \infty) \\ &\simeq \tfrac{1}{2}[E(m = m_p) - E(m \to \infty)] , \end{aligned} \tag{15}$$

which, remarkably, is just the virial theorem for harmonic-oscillator states. Accordingly we can immediately justify the later use of a basic oscillator picture in the description of the structure of the dense phase of protons. These will be key observations in establishing a picture for the proton structure in Sec. IV.

III. THE TWO-COMPONENT SYSTEM

If we transform the Hamiltonian (1) into q space and superimpose two uniform backgrounds of opposite sign and equal density and then take into account the separate interactions, we can easily show that the expectation value of the Hamiltonian is

$$\langle H \rangle = \langle T_e \rangle + \langle T_p \rangle + \tfrac{1}{2} \sum_{\mathbf{q} \neq 0} \frac{4\pi e^2}{V q^2} [\langle \hat{\rho}_e(\mathbf{q}) \hat{\rho}_e(-\mathbf{q}) \rangle - N + \langle \hat{\rho}_p(\mathbf{q}) \hat{\rho}_p(-\mathbf{q}) \rangle - N - 2 \langle \hat{\rho}_e(\mathbf{q}) \hat{\rho}_p(-\mathbf{q}) \rangle] , \tag{16}$$

where the one-particle densities are

$$\hat{\rho}_\alpha(\mathbf{q}) \equiv \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_{i,\alpha}} ,$$

and the averages are taken with respect to the actual ground state of the total system. Note that the $q = 0$ terms are absent by virtue of charge neutrality and the existence of the thermodynamic limit.

We may proceed to the evaluation of (16) by first using the known solutions for each one-component problem [Eq. (12)] and then evaluating the contribution of the coupling between them. Accordingly, we introduce a coupling constant λ into the last term of (1), namely

$$H = (T_e + U_{ee}) + (T_p + U_{pp}) + \lambda U_{ep} ,$$

where the terms in parentheses (with $q=0$ components removed) constitute the separate one-component problems. This Hamiltonian written in q space has the expectation value

$$\langle H\rangle_\lambda=\langle T_e\rangle_\lambda+\langle T_p\rangle_\lambda+\tfrac{1}{2}\sum_{\mathbf{q}\neq 0}\frac{4\pi e^2}{Vq^2}[\langle\hat{\rho}_e(\mathbf{q})\hat{\rho}_e(-\mathbf{q})\rangle_\lambda-N+\langle\hat{\rho}_p(\mathbf{q})\hat{\rho}_p(-\mathbf{q})\rangle_\lambda-N]-\lambda\sum_{\mathbf{q}\neq 0}\frac{4\pi e^2}{Vq^2}\langle\hat{\rho}_e(\mathbf{q})\hat{\rho}_p(-\mathbf{q})\rangle_\lambda \tag{17}$$

where the average $\langle\cdots\rangle_\lambda$, is taken with respect to the ground state at coupling strength λ. For $\lambda=0$ the preceding Hamiltonian is a sum of the two uncoupled one-component parts and the ground state is merely a product of an electronic and a protonic ground state. Correspondingly the energy is given by a sum of two one-component terms, namely

$$\frac{\langle H\rangle_0}{N}=\frac{E}{N}(r_s,m=m_e)+\frac{E}{N}(r_s,m=m_p)\;, \tag{18}$$

which from (12) is now a known function of r_s. This function is plotted (curve 3) in Fig. 2, and it can be seen that it is already a reasonably close approximation to the quantum Monte Carlo results (Fig. 2, curve 4) of Ref. 1.

Now we couple the two systems by increasing λ from 0 to 1, during which the state evolves into the actual ground state of the system (provided that there is no symmetry breaking in either set of degrees of freedom) whose energy will be correctly given by (16). However, by applying the HFT to (17) with respect to λ we find

$$\frac{\partial\langle H\rangle_\lambda}{\partial\lambda}=\left\langle\frac{\partial H}{\partial\lambda}\right\rangle_\lambda=\langle U_{ep}\rangle_\lambda\;, \tag{19}$$

so that $\langle H\rangle$ can be given alternatively by

$$\langle H\rangle=\langle H\rangle_0+\int_0^1 d\lambda\langle U_{ep}\rangle_\lambda$$

or

$$\frac{\langle H\rangle}{N}=\frac{\langle H\rangle_0}{N}-\int_0^1 d\lambda\sum_{\mathbf{q}\neq 0}\frac{4\pi e^2}{Vq^2}\frac{\langle\hat{\rho}_e(\mathbf{q})\hat{\rho}_p(-\mathbf{q})\rangle_\lambda}{N}$$

$$\equiv\frac{\langle H\rangle_0}{N}+\Delta\;, \tag{20}$$

again providing the symmetry remains continuous and there is no level crossing. To calculate the total energy per atom, therefore, we need to determine Δ, which incorporates changes in both potential and kinetic energy [e.g., see Eqs. (48)].

As can be seen from Fig. 2, the difference Δ between the actual total energy and the sum of the two one-component contributions [as calculated with (18) and (12)] will turn out to be small (~ -0.2 Ry) when compared to the one-component contributions ($\simeq 1$ Ry). The quantity Δ, extracted from Ref. 1 and (18), is also plotted in Figs. 3 and 4, where it is compared with the theoretical values obtained as follows: We first acknowledge the enormous difference in the time scales between electrons and protons, which, as noted before, permits us to work within the Born-Oppenheimer or adiabatic approximation. Next, as a first approximation we appeal to linear-response arguments similar to those of Ashcroft and Stroud[21] to calculate the electronic density $\rho_e(\mathbf{q})_\lambda$ induced by a single proton at coupling strength λ later incorporating terms beyond linear response through an effective mass approximation. Because of the Born-Oppenheimer separation the average $\langle\hat{\rho}_e(\mathbf{q})\hat{\rho}_p(-\mathbf{q})\rangle_\lambda$ with respect to the states of the total system can be carried out first with respect to the electronic ground state (for a given proton configuration) and then with respect to the protonic degrees of freedom. The result is that

$$\langle\hat{\rho}_e(\mathbf{q})\hat{\rho}_p(-\mathbf{q})\rangle_\lambda=\langle\langle\hat{\rho}_e(\mathbf{q},\lambda)\rangle_{e(p)}\hat{\rho}_p(-\mathbf{q})\rangle_{\lambda p}\;, \tag{21}$$

again under the assumption that no symmetry is broken as λ is changed. By virtue of the linear-response approximation the number density of the electrons induced by the presence of the particular protonic configuration is given by

$$\langle\hat{\rho}_e(\mathbf{q},\lambda)\rangle_{e(p)}=\lambda|\chi_{\rm scr}(q)|\frac{4\pi e^2}{q^2\epsilon(q)}\hat{\rho}_p(\mathbf{q})\;, \tag{22}$$

where $\chi_{\rm scr}$ is the static electronic response function to the screened field, and $\epsilon(q)$ is the static dielectric function of the electron gas. This expression can be obtained by Fourier transformation of

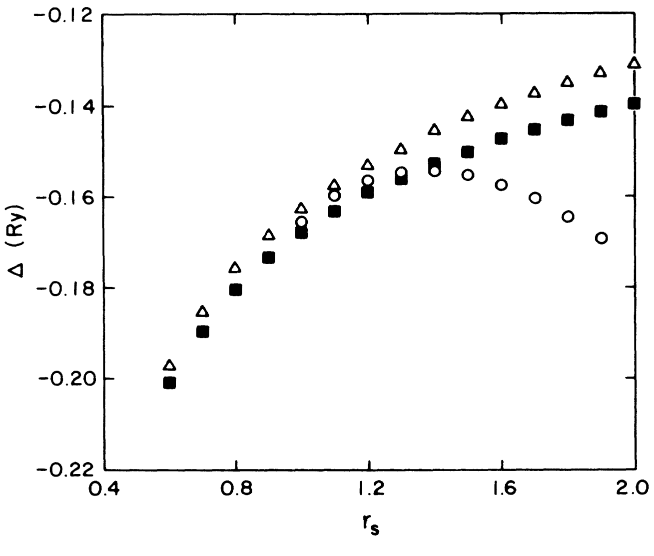

FIG. 3. Results of our calculations for Δ with the PY structure factor (solid squares for the Ichimaru-Utsumi model; triangles for the Geldart-Vosko-Hubbard model of the dielectric function), compared to the actual Monte Carlo values (circles). Note the scale used for Δ.

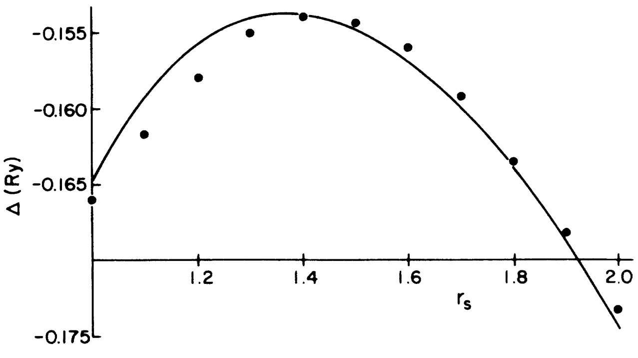

FIG. 4. Final results for Δ [with use of the Ichimaru-Utsumi model for $G(q)$, and the structure factor (41)], for the effective mass ($m_1 = m^*$) shown in curve 3 of Fig. 9.

$$[\hat{\rho}_e(\mathbf{r}_1)]_{e(p)} = \sum_{i=\{p\}} \hat{\rho}_e(\mathbf{r}_1 - \mathbf{r}_i^p)$$
$$= \int d^3r' \hat{\rho}_e(\mathbf{r}_1 + \mathbf{r}') \sum_{i=\{p\}} \delta(\mathbf{r}' + \mathbf{r}_i^p)$$
$$= \int d^3r' \hat{\rho}_e(\mathbf{r}_1 + \mathbf{r}') \hat{\rho}_p(-\mathbf{r}')$$

with the result

$$\langle \hat{\rho}_e(\mathbf{q},\lambda) \rangle_{e(p)} = \langle \hat{\rho}_e(\mathbf{q}) \rangle_\lambda \hat{\rho}_p(\mathbf{q}) ,$$

and also by writing

$$\langle \hat{\rho}_e(\mathbf{q}) \rangle_\lambda = |\chi_{\rm scr}(q)| \lambda \frac{4\pi e^2}{q^2 \epsilon(q)}$$

for the induced electronic number density by a single proton. Combination of (20), (21), and (22) then yields

$$\Delta = -\int_0^1 \lambda d\lambda \frac{1}{V} \sum_{\mathbf{q}\neq 0} \left[\frac{4\pi e^2}{q^2} \right]^2 \frac{|\chi_{\rm scr}(q)|}{\epsilon(q)} \times \frac{\langle \hat{\rho}_p(\mathbf{q}) \hat{\rho}_p(-\mathbf{q}) \rangle_{\lambda p}}{N} , \tag{23}$$

or in terms of the proton-proton partial structure factor ($q \neq 0$) at coupling strength λ

$$S_{pp}(\mathbf{q})_\lambda \equiv \frac{1}{N} \langle \hat{\rho}_p(\mathbf{q}) \hat{\rho}_p(-\mathbf{q}) \rangle_\lambda ,$$

we have

$$\Delta = -\int_0^1 \lambda d\lambda \frac{1}{V} \sum_{\mathbf{q}\neq 0} \left[\frac{4\pi e^2}{q^2} \right]^2 \frac{|\chi_{\rm scr}(q)|}{\epsilon(q)} S_{pp}(\mathbf{q})_\lambda . \tag{24}$$

In the preceding expressions

$$\frac{1}{N} \langle \hat{\rho}_p(\mathbf{q}) \hat{\rho}_p(-\mathbf{q}) \rangle_\lambda$$

refers to a correlation function corresponding to an effective interproton interaction appropriate to an electron-proton coupling at strength λ. Now we make the basic assumption that $S_{pp}(\mathbf{q})_\lambda$ is in fact quite insensitive to λ. This is reasonable, in general terms, from the well-known insensitivity of $S(\mathbf{q})$ to the potential that determines the structure. It is also supported from the previously known fact[4] that S_{pp}, if written in a rescaled form (see Appendix B), changes very little with r_s (for a fixed $\lambda = 1$); a consequence then of the scaling behavior of S_{pp} is that generically S_{pp} will also change very little with λ for a fixed r_s. For consistency with this approximation, we later use a form for S_{pp} that actually has this property.

Under this assumption and in this case of linear response the integration over λ can be carried out giving

$$\Delta = -\frac{1}{2V} \sum_{\mathbf{q}\neq 0} \left[\frac{4\pi e^2}{q^2} \right]^2 \frac{|\chi_{\rm scr}(q)|}{\epsilon(q)} S_{pp}(\mathbf{q}) , \tag{25}$$

which is our result for Δ in this approximation. Now, $\epsilon(q)$ is related to $\chi_{\rm scr}(q)$ by

$$\epsilon(q) = 1 - \frac{4\pi e^2}{q^2} \chi_{\rm scr}(q) , \tag{26}$$

where the dielectric function is normally given within a (static) local-field-correction approach by

$$\epsilon(q) = 1 - \frac{\frac{4\pi e^2}{q^2} \chi_0(q)}{1 + \frac{4\pi e^2}{q^2} \chi_0(q) G(q)} , \tag{27}$$

where

$$\chi_0(q) = -\frac{3n}{2\varepsilon_F} f \left[\frac{q}{2q_F} \right] \tag{28}$$

with

$$f(y) = \tfrac{1}{2} + \frac{1}{4y} (1 - y^2) \ln \left| \frac{y+1}{y-1} \right| \tag{29}$$

being the Lindhard function. Here $\varepsilon_F = \hbar^2 q_F^2 / 2m_e$ with $q_F = (3\pi^2 n)^{1/3}$ and $n = N/V$, and $G(q)$ is the static local field. Because of (25)–(29), the local field $G(q)$ and the structure factor $S_{pp}(q)$ together completely determine Δ in this approximation according to

$$\Delta = \frac{e^2}{\pi} \int_0^\infty dq\, S_{pp}(q) \left[\frac{1}{\epsilon(q)} - 1 \right]$$
$$= \frac{e^2}{\pi} \int_0^\infty dq\, S_{pp}(q) \frac{\frac{4\pi e^2}{q^2} \chi_0(q)}{1 + \frac{4\pi e^2}{q^2} \chi_0(q) [G(q) - 1]} , \tag{30}$$

where we have used the fact that for a homogeneous system $S_{pp}(\mathbf{q}) = S_{pp}(q)$.

We will see later that at lower densities (around and beyond the atomic-molecular transition) we will need to go beyond linear response to account for Δ. Towards this end we will take nonlinearities into account through an effective mass approach for Δ, while still using the linear-response form (30).

IV. MODEL

In what follows, $\chi_0(q)$ and $G(q)$ will be taken from standard treatments of the electron gas problem. Attention therefore focuses on $S_{pp}(q)$, i.e., the static structure factor of a proton system in which the proton-proton interactions fully incorporate electron screening. We start with the following observations: (i) The protons, being comparatively massive, acquire a particular "low-density" structure [in the sense that this would be similar to an electron structure at much lower densities, as is apparent from the scaling properties; see, e.g., (B14)]. This leads to the expected conclusion that symmetry (exchange) effects are not important for the protons, and for this reason a boson picture would also be an acceptable description for them. (ii) The electron screening (which of course has played a crucial role in the acquisition of the proton structure) has the effect of dressing the protonic-plasma oscillations resulting in an acoustic model.[22] We will argue that the structure factor S_{pp} can be replaced by a suitably defined classical function. There are two obvious concerns here, namely the failure of classical functions to reproduce the long-wavelength behavior correctly, and the omission of any recognition of zero-point effects. Both are taken up in what follows, and neither turn out to have any bearing on our results.

As a consequence of (ii) the long-range ground-state behavior of S_{pp} has to reflect this phonon mode by vanishing linearly with q. In addition, as a consequence of (i), we can use the result[23] (which is rigorously true for bosons) that the slope of $S_{pp}(q)$ at small q has to be $\hbar/2m_p c$, where c is the speed of sound. An approximate way to account for this long-range behavior of S_{pp} is to follow the procedure of Chester and Reatto[24] and write the protonic wave function as a product of a short-ranged and a long-ranged (phonon) part

$$\Psi=\Psi_{\mathrm{SR}}\times\Psi_{\mathrm{ph}} .$$

This has the result that

$$S_{pp}(q)=\frac{S_{\mathrm{SR}}(q)}{1+\dfrac{2m_p c}{\hbar q}S_{\mathrm{SR}}(q)e^{-q/q_c}} , \tag{31}$$

where the short-range part $S_{\mathrm{SR}}(q)$ (which we will see is by far the most important) will be determined later. In (31) the sound speed c can be determined with sufficient accuracy for the present application by the Bohm-Staver[22] relation $c^2=(1/3)(m_e/m_p)v_F^2$, that

$$\frac{2m_p c}{\hbar q}=\frac{2}{\sqrt{3}}\sqrt{m_p/m_e}\,\frac{q_F}{q} ,$$

and q_c is a cutoff below which the collective effect occurs (i.e., for $q<q_c$). It is already known[5] that the linear region of $S_{pp}(q)$ around $q=0$, set by q_c, is very small and hardly affects the thermodynamic functions of the system. This conclusion is also in agreement with the Monte Carlo results[25] that are consistent with a quadratic behavior down to $qa \sim 0.6$ (this behavior is reminiscent of a classical hard-core system, as is discussed later). Therefore q_c is very small [an estimate is given in Appendix E, Eq. (E1)], and the dominant part in the proton-proton structure factor for present purposes is $S_{\mathrm{SR}}(q)$.

To find S_{SR} we recall observation (i) above and combine it with the fact that a boson problem can be mapped onto an equivalent classical problem.[26] This is the reason why a classical choice for $S_{\mathrm{SR}}(q)$ works very well as we will see later. However, here we want to be a little more careful and explicitly examine effects arising from the quantum nature of the particles, as manifested in the *local* structure. The main physical consequence (essentially a manifestation of the uncertainty principle) is the zero-point motion of the protons around "classical" sites, which are periodic for a solid phase and disordered in a fluid phase, but in both cases slowly diffusing (the diffusion being exactly zero in the ideal solid). In accordance with this picture we decouple the protonic motion into a slow diffusive part ("dif") later to be described by an essentially classical function, and a local oscillatory part ("LO") describing the zero-point motion around the diffusive centers. As noted before this oscillatory part has already been anticipated [see Eq. (15)] from the scaling results and from the similarity in form between the energy of a proton Wigner crystal and (12). This decoupling leads to the further ansatz

$$\Psi_{\mathrm{SR}}=\Psi_{\mathrm{dif}}\times\Psi_{\mathrm{LO}} ,$$

and its effect on the structure factor S_{SR} can now be discussed in a way that is entirely analogous to any small-oscillations theory, for example the phonon theory for a dynamical solid at $T=0$. We now give a detailed discussion of this model that can be viewed as an approximate method for arriving at a first quantum correction to the classical structure factor.

We assume that the major manifestation of the quantum structure of the protons is through the oscillatory motion of single protons inside "cages" formed by coordination neighbors; the cages are generally diffusive and described as argued before by a classical structure. According to this view point we assign to each proton a coordinate $\mathbf{r}_i=\mathbf{R}_i+\mathbf{u}_i$, where $\mathbf{R}_i$ is a classical (commuting) part, and $\mathbf{u}_i$ the oscillator (noncommuting) part. So, for $q\neq\mathbf{0}$,

$$S(\mathbf{q})=\frac{1}{N}\left\langle\sum_j\sum_{j'}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}e^{i\mathbf{q}\cdot\mathbf{u}_j}e^{-i\mathbf{q}\cdot\mathbf{u}_{j'}}\right\rangle ,$$

where the average denotes

$$\langle\cdots\rangle=\langle\langle\cdots\rangle_{\mathrm{LO}}\rangle_{\mathrm{cl}} ,$$

With the average over local oscillations ("LO") being carried out before the remaining average over an equivalent classical system ("cl"). Then separating $j=j'$ and $j\neq j'$ terms we have

$$S(\mathbf{q})=1+\frac{1}{N}\left\langle\sum_j\sum_{j'\neq j}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}e^{i\mathbf{q}\cdot\mathbf{u}_j'}e^{-i\mathbf{q}\cdot\mathbf{u}_{j'}}\right\rangle , \tag{32}$$

and by doing only the average with respect to the local quantum oscillators we obtain the result[27]

$$S(\mathbf{q})=1+\frac{1}{N}\left\langle\sum_j\sum_{j'\neq j}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}e^{-q^2\rho_{j-j'}^2}\right\rangle_{\mathrm{cl}} ,$$

where

$$\rho_{j-j'}^2=\frac{1}{Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}\{(n_{\mathbf{k}}+\tfrac{1}{2})[1-\cos\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})]$$
$$-i\sin\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})\}$$

and where $n_{\mathbf{k}}$ is the phonon occupancy for wave number $\mathbf{k}$ and polarization parallel to $\mathbf{q}$. Now at $T=0$ we have $n_{\mathbf{k}}=0$ for all $\mathbf{k}$ (i.e., only zero-point motion) and so we have

$$S(\mathbf{q})=1+\frac{1}{N}e^{-2W}\left\langle \sum_j\sum_{j'\neq j}\exp\left[i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})+\frac{q^2}{2Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\right]\right\rangle_{\mathrm{cl}},$$

where

$$2W=q^2\frac{1}{2Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}\,. \tag{33}$$

Now if we expand around $q^2=0$ we obtain the standard sum over multiple-phonon contributions, multiplied overall by a Debye-Waller factor, namely

$$S(\mathbf{q})=1+\frac{1}{N}e^{-2W}\left\langle \sum_j\sum_{j'\neq j}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\left[1+\frac{q^2}{2Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}+\frac{1}{2!}\left[\frac{q^2}{2Nm_p}\right]^2\left[\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\right]^2+\cdots\right]\right\rangle_{\mathrm{cl}}. \tag{34}$$

But according to our physical interpretation

$$1+\frac{1}{N}\left\langle\sum_j\sum_{j'\neq j}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\right\rangle_{\mathrm{cl}}=S_{\mathrm{cl}}(\mathbf{q}) \tag{35}$$

so that $S(q)$ can be easily shown to be

$$S(\mathbf{q})=1+e^{-2W}\left[(S_{\mathrm{cl}}(\mathbf{q})-1)+\frac{q^2}{2Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}[S_{\mathrm{cl}}(\mathbf{q}+\mathbf{k})-1]+\frac{1}{2!}\left[\frac{q^2}{2Nm_p}\right]^2\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\frac{\hbar}{\omega_{\mathbf{k}}}\frac{\hbar}{\omega_{\mathbf{k}'}}[S_{\mathrm{cl}}(\mathbf{q}+\mathbf{k}+\mathbf{k}')-1]+\cdots\right],$$

or finally

$$S(\mathbf{q})=e^{-2W}\left[S_{\mathrm{cl}}(\mathbf{q})+\frac{q^2}{2Nm_p}\sum_{\mathbf{k}}\frac{\hbar}{\omega_{\mathbf{k}}}S_{\mathrm{cl}}(\mathbf{q}+\mathbf{k})+\frac{1}{2!}\left[\frac{q^2}{2Nm_p}\right]^2\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\frac{\hbar}{\omega_{\mathbf{k}}}\frac{\hbar}{\omega_{\mathbf{k}'}}S_{\mathrm{cl}}(\mathbf{q}+\mathbf{k}+\mathbf{k}')+\cdots\right]. \tag{36}$$

Equation (36) shows how we can derive in a very straightforward way the quantum-mechanical structure factor at $T=0$ for this model. The choice $S_{\mathrm{cl}}(\mathbf{q})=N\sum_{\mathbf{K}}\delta_{\mathbf{q},\mathbf{K}}$ corresponds to the case of completely nondiffusive periodic sites (a solid with reciprocal lattice vectors $\mathbf{K}$) and in this case we have to sum (36) to all orders since coherence effects are important. In our case of diffusive cages we will take for the moment the approximation

$$S_{\mathrm{cl}}(\mathbf{q})=S^{\mathrm{PY}}(\mathbf{q})\,, \tag{37}$$

where $S^{\mathrm{PY}}(\mathbf{q})$ is the Percus-Yevick (PY) solution[28] to the underlying equivalent classical problem. The assumption here is that the particular zeroth-order approximation to the earlier model (namely no zero-point corrections), which at the same time is reasonably capable, as we will see, of giving the correct one-component protonic term (12), is the Percus-Yevick approximation.[29] Two other reasons for choosing the PY model are, as we will see, that the first peaks occur close to those for a bcc solid phase, and also that S^{PY} in its rescaled form [i.e., $S^{\mathrm{PY}}(\bar{\mathbf{q}})$] does not depend on r_s at all [see Eq. (38) later]. It can serve therefore as a satisfactory candidate for a structure factor that displays insensitivity to λ, according to (B18). Moreover, because of the action of electronic screening (which changes the soft Coulomb interaction into a potential that is more steeply repulsive at short range), S_{pp} will be modeled as the structure factor for impenetrable spheres of diameter σ. Accordingly, by these arguments σ is directly related to the choice of variational function in Ψ_{SR} (but in addition involves some manifestation of the oscillator state as we will discuss later).

From the definition of the direct correlation function c of the equivalent fluid, we have

$$S^{\mathrm{PY}}(q)=\frac{1}{1-nc(q\sigma)}\,, \tag{38}$$

where for the hard-sphere case ($y=q\sigma$), the solution for c is[28]

$$c(y)=-4\pi\sigma^3\left[\frac{24\gamma}{y^6}-\frac{2\beta}{y^4}+(\sin y)\left[\frac{\alpha+2\beta+4\gamma}{y^3}-\frac{24\gamma}{y^5}\right]\right.$$
$$+(\cos y)\left[\frac{-\alpha-\beta-\gamma}{y^2}\right.$$
$$\left.\left.+\frac{2\beta+12\gamma}{y^4}-\frac{24\gamma}{y^6}\right]\right],$$

with

$$\alpha=\frac{(1+2\eta)^2}{(1-\eta)^4},\quad \beta=\frac{-6\eta(1+\eta/2)^2}{(1-\eta)^4},\quad \gamma=\frac{\eta}{2}\alpha\ .$$

Here the packing fraction η is defined by

$$\eta=\frac{n\pi\sigma^3}{6}\ .$$

This form for S_{pp} has been shown[30] to describe the static structure of liquid metals reasonably well for $\eta\sim0.4$–0.5, especially the first peak (Fig. 5). In our case the first peak dominates the contribution to Eq. (30) because $S_{pp}(q)\to1$ as $q\to\infty$, and $\rho_e(q)$ [or $1/\epsilon(q)-1$] drops as q increases. In fact, in the $q\to\infty$ limit it must have a $1/q^4$ behavior according to the cusp condition,[31] which in q space reads

$$\frac{N}{V}+\int\frac{d^3q}{(2\pi)^3}\rho_e(q)=\frac{a}{16\pi}\lim_{q\to\infty}[q^4\rho_e(q)]\ .$$

To obtain consistency with our use of (12) for the proton gas (and with our assumption of a λ-independent structure) we impose expression (12) on the energy of the protons calculated using the model S_{pp}. In this way we determine the appropriate packing fraction η to be used for the structure of the proton fluid in this model. For example, we may roughly estimate η by combining the exact solution[32] (within the Percus-Yevick theory)

$$E_M=\tfrac{1}{2}\sum_{q\neq0}\frac{4\pi e^2}{Vq^2}[S_{pp}^{\rm PY}(q)-1]$$
$$=\frac{-6\eta^{2/3}}{r_s}\left[\frac{1-\frac{\eta}{5}+\frac{\eta^2}{10}}{1+2\eta}\right]\ \text{Ry/proton} \tag{39}$$

with Eq. (14). We conclude then that an appropriate packing fraction for the PY protons is[33]

$$\eta\simeq0.41\ . \tag{40}$$

This value is reasonable, given that classical fluids correspond to $\eta\sim0.46$, whereas a fit to highly quantum-fluid helium[30] gives $\eta\sim0.25$. A corresponding $S_{pp}^{\rm PY}(q)$ for $r_s=1.3$ is shown in Fig. 5. As a further experimental justification of the use of this classical S_{pp} we cite the case of ^{3}He, where the closed form (38) as shown in Fig. 6, can be brought quite close to the experimental values.[34] In addition, the rather significant departure of the classical $S(q)$ at low q from the experimental curve for ^{3}He (Fig. 6) does not occur for hydrogen because of the higher η that results in $\lim_{q\to0}S_{pp}(q)\sim0.03$, i.e., much closer to zero (see the discussion in Appendix E). For a further discussion on the relation of Δ, as calculated with the classical structure factor, and proton-proton correlation, as well as on a variational argument based on the Gibbs-Bogolyubov inequality that provides a *rigorous upper bound* for the exact Δ and the total energy, see Appendix D.

Proceeding to the next order correction to (36) (which now includes the zero-point oscillations) we retain only the zero-phonon term in the expansion (34). This gives, in view of (35),

$$S(\mathbf{q})\equiv1+\frac{1}{N}e^{-2W}\left\langle\sum_j\sum_{j'\neq j}e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\right\rangle_{\rm cl}$$
$$=e^{-2W}S_{\rm cl}(\mathbf{q})+1-e^{-2W}\ , \tag{41}$$

which is the form of the structure factor that we will use for the final results. This approximation is equivalent to ignoring correlation [i.e., to setting $S_{\rm cl}(\mathbf{q}+\mathbf{k})=1$ for

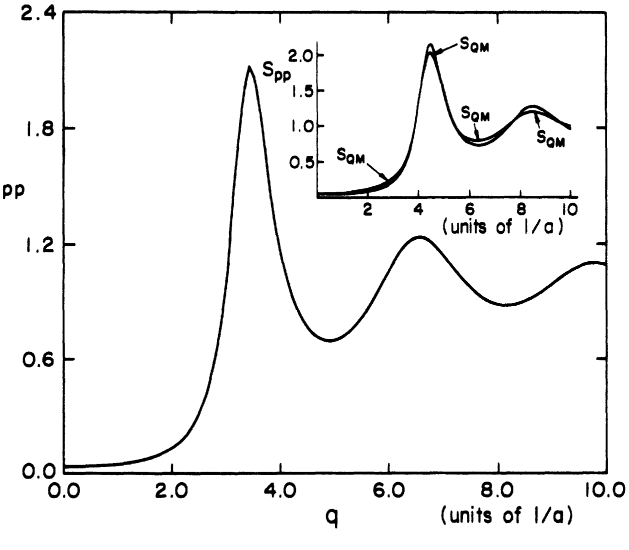

FIG. 5. Percus-Yevick structure factor for $r_s=1.3$ (or $q_F\simeq1.48a^{-1}$) and $\eta=0.4088$. The corrected structure factor (41) used in the final results compared to the corresponding PY structure factor at $r_s=1$ is also shown in the inset.

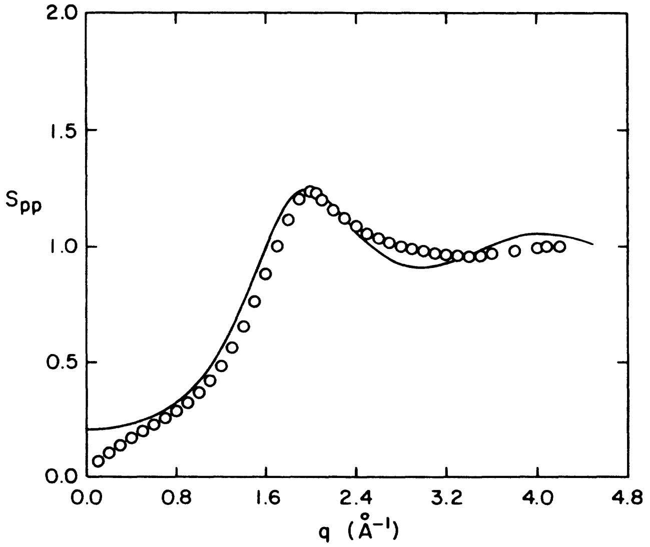

FIG. 6. Comparison of the experimental (Ref. 34) $S(q)$ (circles) for ^{3}He with the Percus-Yevick $S^{\rm PY}(q)$ corresponding to $\sigma=0.3041$ Å, $\eta=0.20$.

every **k**] in all higher-order terms of (36). Physically, it is also equivalent to the assumption that the oscillations on different diffusive sites are uncorrelated, which except for very small q (the case handled by the phonon term in $\Psi=\Psi_{\mathrm{SR}}\times\Psi_{\mathrm{ph}}$), is an excellent assumption for a disordered phase, since there is no phase coherence. (It is less appropriate for the solid phase but we shall nevertheless assume that the higher-order contributions are adequately included in the highly correlated structure of S_{cl}, most particularly in the first peak which, as noted before, is close to the corresponding one for a bcc lattice.) In fact, we could have obtained (41) directly from (32) simply by carrying out the quantum oscillator (QO) averages separately for each oscillator and using[35]

$$\langle e^{i\mathbf{q}\cdot\mathbf{u}_j}\rangle_{\mathrm{QO}}=e^{-(1/2)\langle(\mathbf{q}\cdot\mathbf{u}_j)^2\rangle}$$

and the assumption that each such factor is the same for all cages j, each having a common average value equal to $e^{-(1/6)q^2\langle u^2\rangle}$. The results of such a procedure give exactly (41) with $2W=\frac{1}{3}q^2\langle u^2\rangle$. The main consequence of (41) is that because of the presence of the Debye-Waller factor, the oscillations in $S(\mathbf{q})$ damp out more quickly than is the case for the corresponding classical fluid. This means that the classical structure factor will show higher correlations than those actually found in a quantum-mechanical system. This is consistent with the experimental data in Fig. 6 (and also with the discussion in Appendix D).

Next, to be consistent with the preceding assumption of uncorrelated oscillations we adopt an Einstein model, namely $\omega_{\mathbf{k}}=\omega_0$ for every **k**. In this case we have from (33) that

$$\frac{2W}{q^2}=\frac{\hbar}{2Nm_p\omega_0}\sum_{\mathbf{k}}1=\frac{\hbar}{2m_p\omega_0}$$
$$=\frac{m_e}{(m_e+m_p)}\frac{a^2}{\hbar\omega_0/(e^2/2a)}\ . \tag{42}$$

The frequency ω_0 in a simple ion-sphere model for the solid[19] is easily calculated from the harmonic potential

$$U=-\left[3-\left[\frac{r}{r_s a}\right]^2\right]\frac{1}{r_s}\ \mathrm{Ry}$$

with the result

$$\hbar\omega_0=\left[\frac{m_e}{m_p}\right]^{1/2}\frac{\sqrt{2}}{r_s^{3/2}}\ \mathrm{Ry} \tag{43}$$

or from a more accurate perturbative analysis[20] rescaled to a proton Wigner crystal, with the result

$$\hbar\omega_0=\left[\frac{m_e}{m_p}\right]^{1/2}\frac{5.3}{r_s^{3/2}}\ \mathrm{Ry}\ . \tag{44}$$

However, to be consistent with the use of our liquid S_{pp}, we will determine ω_0 from the VWN expression (12) for $m=m_p$, as follows.

According to our discussion leading to (15), ω_0 is related to the zero-point energy of an oscillator and so it can be determined by

$$\frac{\hbar\omega_0}{2}\simeq\frac{E(m=m_p)}{N}-\frac{E(m\to\infty)}{N}$$

and also use of (12) and (13). The resulting density-dependent ω_0 again goes as $\sim 1/(r_s^{3/2}m_p^{1/2})$ and is shown in Fig. 7, where it is compared with (44). The resulting *rms* displacements $(\langle u^2\rangle)^{1/2}$ are shown in Fig. 8. As a result, the final form of $S(\mathbf{q})$ from (41) and (42) is shown in the inset of Fig. 5, where it is compared with $S^{\mathrm{PY}}(\mathbf{q})$ [Eq. (38)].

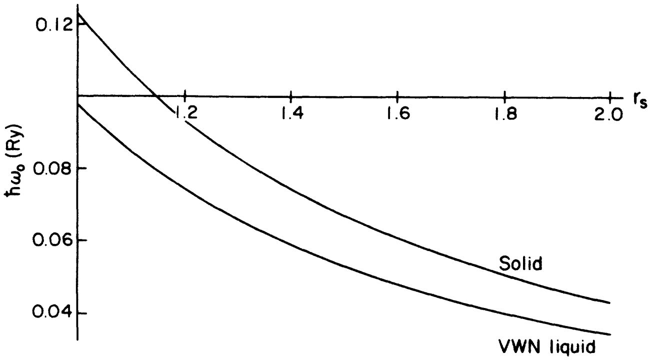

FIG. 7. Natural frequency ω_0 of the Einstein oscillators, in the cage-model correction for the structure factor plotted vs r_s.

This "cage-model" correction to $S_{pp}(q)$ gives a better justification of the procedure for determining the appropriate η described for the PY case (where the energy is only potential energy). As noted, we can absorb the zero-point kinetic energy of the proton system into the oscillatory part and ultimately into the appropriate effective σ (in a variational context we would have σ as a variational parameter in, e.g., a Jastrow ansatz, or equivalently in a classical structure factor [see Appendix D)]; it also follows that if we wish to approximate the highly anharmonic solid with our continuous approximation, we must set the small kinetic energy due to diffusion to zero and hence equate the resulting effective E_M (that includes the zero-point kinetic energy) to the total energy of the protonic component. In this case these corrections increase the appropriate values of η [consistent with (12)] to ~ 0.43 at $r_s=1$ up to ~ 0.45 at $r_s=2$. This enhance-

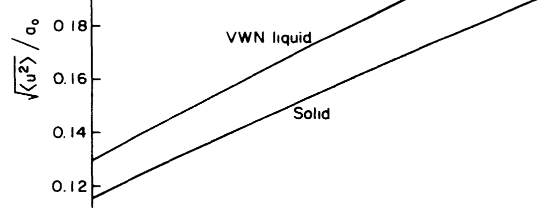

FIG. 8. Resulting rms displacement around the cages, vs r_s [in units of the actual Bohr radius $a_0=a/(1+m_e/m_p)$].

ment of σ is attributed in part to the zero-point motion of the particles. For those values of η, the first peak of the structure factor (41) occurs at $qa \sim 4.46/r_s$ (see Fig. 5), which remains close to the first peak for the sphericalized structure factor for a bcc phase occurring at $qa \sim 4.38/r_s$.

It is important to emphasize that the largest part of the physics sensitive to the proton structure factor is expected to be described by the one-component protonic term (12). Indeed the results we discuss in the next section do not seem to be very sensitive to the accuracy with which we determine the various corrections to $S_{pp}(\mathbf{q})$ as this is used in (30). The last result is not obvious and it was therefore important that the corrections themselves were discussed in some detail.

We turn now to electronic considerations. For the local-field correction $G(q)$ we have used for the sake of comparison two quite different approximations: (i) the Geldart-Vosko modification of the Hubbard form for $G(q)$,[36] and (ii) the more accurate parametrized expression for $G(q)$ of Ichimaru and Utsumi[37] (for details see Appendix C). The results for Δ for the simplest PY model are very good at high densities ($r_s \sim 1$, see Fig. 3) and are discussed in the next section together with the results of our use of the corrected structure factor (41). They show that both models for the local field are reasonably good, although the Ichimaru-Utsumi model is a little more satisfactory and we will continue with this model from this point on.

Finally the results of the next section will also show that an attempt to go beyond linear response through an approximate effective-mass argument is even more satisfactory in accounting for the behavior of Δ at lower densities (around and beyond the atomic-molecular transition). The mass dependence of Δ, necessary for such an approach, is determined through the use of the general scaling property (9) as follows.

The dependence of Δ on the two masses m_1, m_2 can be determined by imposing the scaling properties (9) and (11) on (20). The general result is that

$$\Delta = \frac{f(m_1 r_s; m_2 r_s)}{r_s} \ . \tag{45}$$

Now in our model

$$\Delta = -\int_0^1 d\lambda \frac{1}{V} \sum_{\mathbf{q}\neq 0} \frac{4\pi e^2}{q^2} \langle \hat{\rho}(\mathbf{q}) \rangle_\lambda S_{pp}(\mathbf{q}) \ , \tag{46}$$

where in linear response

$$\langle \hat{\rho}(\mathbf{q}) \rangle_\lambda = \frac{\lambda \dfrac{q_0^2}{q^2} f(q/2q_F)}{1 + \dfrac{q_0^2}{q^2} f(q/2q_F)[1 - G(\mathbf{q})]}$$

and where $q_0^2 = 4\pi e^2 3n/2\varepsilon_F$ is the Thomas-Fermi wave vector. Accordingly the dependence of Δ on m_2 is only through $S_{pp}(\mathbf{q})$, but the dependence on m_1 is both through q_0^2 and $G(\mathbf{q})$ [and generally through $S_{pp}(q)$ as well].

If we now rescale according to $\mathbf{q} = \bar{\mathbf{q}}/r_s a$, our structure factor (41) is a function of $m_2 r_s$ according to (B18) [or in general it is also a function of $m_1 r_s$ according to (B14)]. This also follows directly from (42), where we have

$$\frac{2W}{q^2} \sim \frac{r_s^{3/2}}{m_p^{1/2}} \Longrightarrow e^{-2W} \sim e^{-\mathrm{const}/(m_p r_s)^{1/2}}$$

and from the fact that, as noted before, $S^{\mathrm{PY}}(\mathbf{q})$ does not depend on r_s after the preceding rescaling of $\mathbf{q}$ is carried out, and it does not depend on m_p either. As for the dependence on m_1, we note that according to (45) we can determine the value of Δ for an arbitrary value of m_1 by the consecutive substitutions $\mathbf{q} \to \bar{\mathbf{q}}/r_s a$, then $r_s \to r_s m_1/m_e$, and finally $\bar{\mathbf{q}} \to \mathbf{q} r_s a$ into $r_s \Delta$ as this is determined by (46) [or (30)]. It remains therefore to determine the appropriate effective mass m^* for the electrons in the low-density regime and to use $m_1 = m^*$ in Δ. This can be done in the context of a tight-binding (TB) approach as we will now discuss.

Essentially it is necessary to describe in single-particle terms the electron-proton interaction in metallic monoatomic hydrogen. As a first step, we expect that the most reasonable one-electron Hamiltonian in the metallic regime will involve a potential $U(\mathbf{r}) = \sum_{\mathbf{R}} u(\mathbf{r} - \mathbf{R})$, where u is a screened potential. The corresponding simplest "single-atom" picture is the solution of an one-electron problem in a Thomas-Fermi potential. The orbitals for the TB analysis should therefore be those of the Yukawa potential, and correspondingly the whole approach should be physically valid at low enough densities so that there can exist bound states of the Yukawa potential. By "low enough" we mean for $r_s \geq r_{s0}$, where r_{s0} is the Mott point where the lowest bound state has zero energy, i.e., merges into the continuum. For a particle in a Yukawa potential $u(r) = (-e^2/r)e^{-q_0 r}$, the first zero-energy bound state is numerically known to appear[38] for a screening wave vector

$$q_0(r_{s0}) = \frac{1}{0.839\,91 a_0} \ ,$$

which is equivalent to an $r_{s0} = 1.72$. Accordingly we expect a TB analysis of the equivalent one-electron problem to be approximately valid for $r_s > 1.72$. An example of such an analysis for a simple cubic structure (sc) of side R gives an energy[39]

$$E_{1s}(\mathbf{k}) - \mathrm{const} \simeq -2I(R)(\cos k_x R + \cos k_y R + \cos k_z R) \ ,$$

or as $k \to 0$,

$$E_{1s}(k) - \mathrm{const} \simeq R^2 k^2 I(R) \ ,$$

where $I(R)$ is the energy-overlap integral

$$I(R) = -\int \Phi_{i+1}^* \Delta U \Phi_i d^3r \ .$$

Equating this to $\hbar^2 k^2/2m^*$ we obtain

$$\frac{m^*}{m_e} = \frac{\hbar^2}{2m_e R^2} \frac{1}{I(R)} \ ,$$

or with $R = r_s a(4\pi/3)^{1/3}$ for a sc structure, we get

$$\frac{m^*}{m_e} = \left[\frac{3}{4\pi}\right]^{2/3} \frac{1}{r_s^2} \frac{e^2/2a_0}{I(r_s)} \; .$$

The required overlap integral $I(R)$ for an unscreened Coulomb potential and with 1s states can be found exactly by using prolate-spheroidal coordinates,[40] and summing for this case three kinds of integrals. The result is given by[39]

$$I(R) = \left[\tfrac{3}{2}\left[1+\frac{R}{a}\right] + \tfrac{1}{6}\left[\frac{R}{a}\right]^2\right] 2e^{-R/a}\,\text{Ry}$$

for $R > 5a_0$ (i.e., above the Mott transition point). However, we reemphasize that in our application the densities of interest are much higher, and furthermore we wish to carry out an analysis that would approximate a screened Coulomb potential. Towards this end we take advantage of the general form of the structure of I, namely

$$I \sim \int d^3r \frac{e^{-r/a}}{a^{3/2}} \frac{e^2}{\bar{r}} e^{-q_{\text{TF}}\bar{r}} \frac{e^{-r'/a}}{a^{3/2}} \; ,$$

where $\mathbf{r}$, $\mathbf{r}'$, or $\bar{\mathbf{r}}$ denotes the integration variable as referred to different centers. Using this structure we approximate it by a two-center integral, namely

$$I \sim \int d^3r \frac{e^{-r(1/a+q_{\text{TF}}/2)}}{a^{3/2}} \frac{e^2}{r} \frac{e^{-r'(1/a+q_{\text{TF}}/2)}}{a^{3/2}} \; .$$

This is equivalent to an energy-overlap integral for an unscreened potential, but now with the replacement

$$a \rightarrow \frac{a}{1+\bar{q}_0/2r_s^{1/2}}$$

and also multiplied by an additional factor $1/(1+\bar{q}_0/2r_s^{1/2})^3$, where we have written $q_{\text{TF}} \equiv \bar{q}_0/r_s^{1/2}a$. It follows that we can again use the same expression for $I(R)$ for this case, but with the aforementioned adjustments. The final result for m^*/m_e gives the effective mass shown in Fig. 9 (curve 1). In a band-structure sense, this effective mass approach is the simplest way of including terms going beyond linear response.

In contrast to the preceding TB argument, which is appropriate at sufficiently low densities, we can use a spherical-cell method[41] in combination with Bardeen's[42] approximation for the determination of the effective mass at high densities. The result of such an approach, valid for high densities ($r_s < r_{s0}$), gives $m^* \sim m_e$ (with more precision we obtain $m^*/m_e = 1.01$ at $r_s = 1$, up to $m^*/m_e = 1.06$ at $r_s = 2$, see Fig. 9, curve 2).

In accordance with the preceding we propose a smooth interpolation between the high-density regime to the TB regime, the crossover occurring around $r_s \sim 1.7$. This interpolation shown in Fig. 9 (curve 3) determines the effective mass that is used in Δ, and gives the results for Δ shown in Fig. 4. Again the effect of these corrections on Δ is rather small at high densities: linear response is now seen to be particularly well justified in $1 \le r_s < 1.4$. This might have been anticipated for crystalline phases from the value of $U(k)$ at $k \sim 2q_F$ which, for a Thomas-Fermi potential

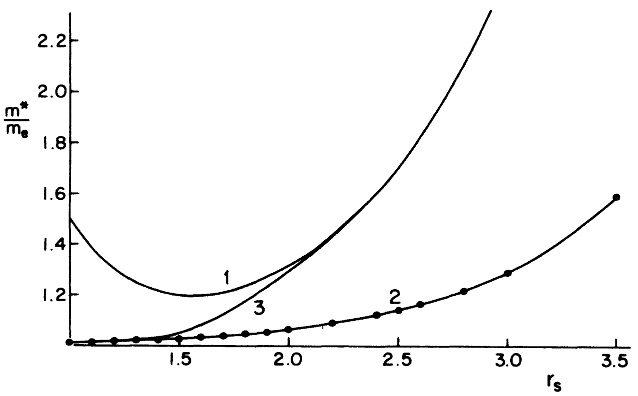

FIG. 9. Effective electronic mass m^*, as given by a TB approach (curve 1) and by a spherical cell method appropriate for high densities (curve 2). An interpolation between the high-density regime and TB regime is also shown (curve 3) that was actually used for the final results.

$$U(k) = n\frac{4\pi e^2}{q^2+q_0^2}$$

turns out to be

$$\sim \frac{3}{8r_s} \frac{1}{1+0.166r_s}\,\text{Ry} \; ;$$

as a result the ratio $U(k)/\varepsilon_F$ is $\sim 0.1 r_s$.

V. RESULTS AND DISCUSSION

We have determined Δ by numerically integrating Eq. (30) for the models discussed in the preceding section. The results for the Percus-Yevick structure factor are shown in Fig. 3 (and the corresponding total energy is shown in Fig. 10). Note that as anticipated the Ichimaru-Utsumi form for the local-field correction is more satisfactory (and is also more consistent with our use of the Monte Carlo results for the electron gas). Not only do we obtain the expected order of magnitude for Δ, we actually obtain very close agreement with the Monte Carlo results[1] in the metallic range $1 \le r_s < 1.4$ despite the approximations used. This shows essentially that the largest contribution to the total energy that comes from the two one-component parts of the Hamiltonian for this range of r_s has been successfully accounted for by the systematic use of the virial and the Hellman-Feynman theorems.

The results for Δ, with the corrected structure factor (41) (for quantum effects) of the preceding section, are almost identical to the ones shown in Fig. 3, the resulting total energy being shown in Fig. 11, curve 1. The small disagreement for $r_s > 1.4$ (which is less than 0.04 Ry at the highest r_s available Monte Carlo calculation at $r_s = 2$) is attributable to increasing inadequacy of the linear-response argument. As we see, however, it is only at the lowest metallic densities (close to and beyond the atomic-molecular transition at $r_s \sim 1.4$ according to the Monte Carlo results[1]) that the nonlinearities (omitted from the two one-component terms) arising from the cross-interaction term between protons and electrons become important. We showed in the preceding section an

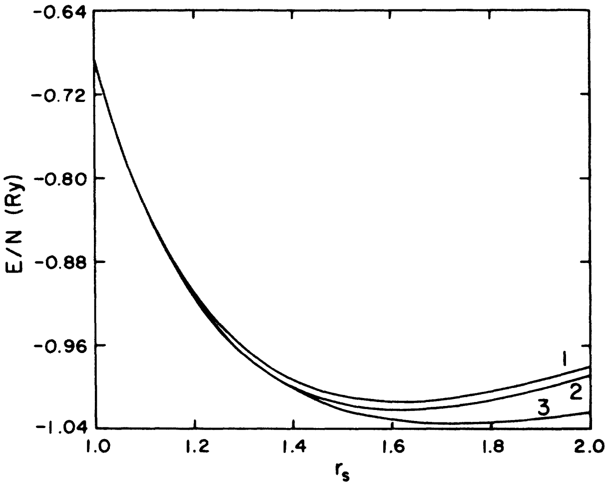

FIG. 10. Total energy per atom based on a fit to the Geldart-Vosko-Hubbard model (curve 1) and to the Ichimaru-Utsumi model (curve 2) compared to the expression (47) (curve 3) (see text).

effective-mass approach to account for those residual effects in Δ. The results of this approach are also shown in Fig. 4, showing very good agreement with the entire range of the Monte Carlo results. Although we have used a continuous structure, we have merely set the diffusive kinetic energy to zero, in order to approximately represent the solid in an average way. More accurately, we have exploited the fact that a liquid metallic phase of hydrogen is very close energetically to a solid phase,[8] the difference being a few mRy; the result is now a very simple model to describe hydrogen.

It might be asked why a phase of continuous symmetry was used for the one-component proton problem, rather than, say, the Wigner crystal. The reason rests mainly in our goal for internal consistency with the scaling relations and the use of a liquid structure factor. However, it can be shown (see Fig. 11, curve 2) that the final results from using such an alternative procedure are again close to the Monte Carlo results (less than 1% lower only in the highest densities), which generally provide an upper bound to the actual total energy.

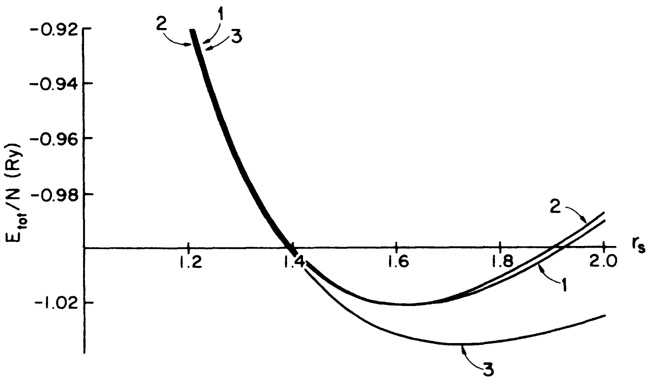

FIG. 11. Total energy (for the bare electronic mass) based on a Wigner crystal one-component term (curve 2) as compared to our VWN results (curve 1) and to the Monte Carlo total energy.

If we assume that our scheme remains correct at higher densities ($r_s < 1$), then from the virial theorem alone we can predict the equation of state for metallic hydrogen using only a single numerical integration for Δ and the closed-form formulas for the one-component terms of the Hamiltonian. In this respect, we also determine therefore an appropriate fit of the numerically found values of Δ in the Ichimaru-Utsumi model for $0 < r_s \leq 2$, so that by using Eq. (20) we arrive at an approximate closed-form expression for the total energy that we plot in Fig. 12. For comparison we have also plotted the curve

$$\frac{2.21}{r_s^2}-\frac{2.707\,22}{r_s}+d_1+d_2r_s+d_3r_s^2\;, \tag{47}$$

with $d_1=-0.2166$, $d_2=0.0566$, $d_3=-0.0301$ which is supposed to describe[1,43] in rydbergs the Monte Carlo results for the total energy per atom for $1 \leq r_s \leq 2$. We observe that our results are consistent with an extension of the same curve into higher densities. [As already mentioned, the lower density results ($r_s > 1.4$) can be reproduced by an effective mass approach.]

In order to determine the equation of state from this approximate expression, we proceed as follows: from the VT [Eq. (5)] we can derive exact results for the kinetic energy $\langle T \rangle$ and the potential energy $\langle U \rangle$ of a general Coulomb system in terms of its total energy E, namely

$$\langle T \rangle = -\frac{d}{dr_s}(Er_s)$$

and (48)

$$\langle U \rangle = \frac{1}{r_s}\frac{d}{dr_s}(Er_s^2)\;.$$

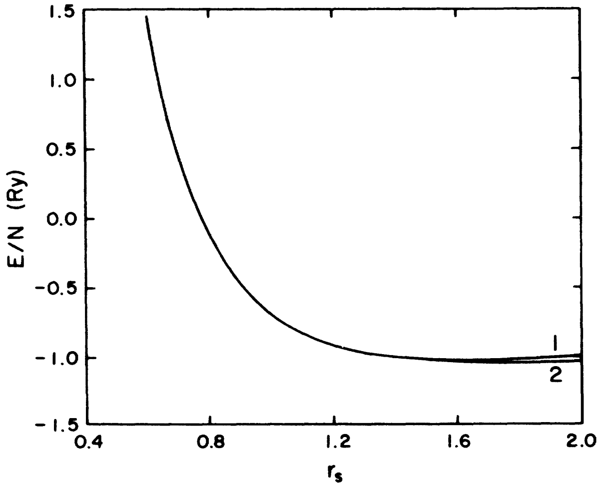

FIG. 12. Extension of the total energy per atom at higher densities, based on a fit to the Ichimaru-Utsumi model and the PY structure factor (curve 1), compared to the expression (47) (curve 2).

The combination of these expressions and equations (20) [or (47)] and (5) gives the equation of state $p(r_s)$ of metallic hydrogen, which turns out to be

$$p(r_s)=\frac{1}{4\pi}\left[\frac{4.42}{r_s^5}-\frac{2.707\,22}{r_s^4}-\frac{d_2}{r_s^2}-\frac{2d_3}{r_s}\right]\left[\frac{e^2}{2a^4}\right],$$

where $e^2/2a^4 \simeq 14\,700$ GPa is the atomic unit of pressure.

VI. CONCLUSIONS

By applying general theorems to a Coulomb system we have derived exact scaling properties regarding the mass and charge dependence of its energy and structure factors. We have then used these properties and worked within a model of the two-component system that accurately produces the Monte Carlo results for metallic hydrogen. Essentially, in this paper we have provided a method that accurately derives the Monte Carlo results for metallic hydrogen by starting from the well-known Monte Carlo treatment of the electron-gas problem. We have therefore arrived at a new model for the energetics of the metallic phase of hydrogen that is valid to very good approximation, apparently even beyond the point of the transition to the molecular state (which is at about $r_s \sim 1.4$ according to the Monte Carlo results). With the use of a different mass for the ionic component we can also determine, with the same method, the equation of state of an electron-hole liquid for an arbitrary mass ratio m_e/m_h, provided that this is small enough for the Born-Oppenheimer approximation to be reasonably valid. More generally, by using the dependence of the energy on the ionic charge, namely Eq. (A7) of Appendix A in place of Eq. (12), we can determine, with the same method, the equation of state for an arbitrary dense Coulombic two-component system.

ACKNOWLEDGMENTS

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APPENDIX A

Here we generalize (12) for the energy of a one-component system in the case of particles of arbitrary charge Ze. We also give another exact scaling property of the general two-component system for particles of arbitrary charges Z_1 and Z_2. First, we introduce a coupling constant λ in the one-component Hamiltonian, namely

$$H=T+\lambda U\ .$$

Then the HFT with respect to λ gives the Pauli theorem, namely

$$\frac{\partial\langle H\rangle_\lambda}{\partial\lambda}=\left\langle\frac{\partial H}{\partial\lambda}\right\rangle_\lambda=\langle U\rangle_\lambda\equiv U_\lambda\ . \tag{A1}$$

Correspondingly, carrying out the differentiation with respect to r_s, the virial theorem is now modified to read

$$3p_\lambda V=2T_\lambda+\lambda U_\lambda\ . \tag{A2}$$

Combination of (A1) and (A2) with $E_\lambda=T_\lambda+\lambda U_\lambda$ yields

$$\lambda\frac{\partial E_\lambda}{\partial\lambda}=2E_\lambda-3p_\lambda V\ , \tag{A3}$$

which together with

$$p_\lambda=-\frac{r_s}{3V}\frac{\partial E_\lambda}{\partial r_s} \tag{A4}$$

gives

$$r_s\frac{\partial E_\lambda}{\partial r_s}-\lambda\frac{\partial E_\lambda}{\partial\lambda}=-2E_\lambda\ . \tag{A5}$$

This is also an exact partial differential equation for the internal energy at coupling strength λ. Its general solution is found to have the scaling form

$$E_\lambda(r_s)=\frac{f(\lambda r_s)}{r_s^2}\ . \tag{A6}$$

This general property can be combined with (11) for the energy of a one-component system of particles of arbitrary mass m and charge Ze. For example, by imposing (A6) on (12) and setting $\lambda=Z^2$ we obtain the expression

$$\begin{aligned}\frac{E}{N}(r_s,m,Z)=\frac{AZ^4}{x}\Bigg\{&\ln\left[\frac{r_s}{r_s+\frac{b}{Z}x^{1/2}r_s^{1/2}+\frac{c}{Z^2}x}\right]+\frac{2b}{Q}\tan^{-1}\left[\frac{\frac{Q}{Z}x^{1/2}}{2r_s^{1/2}+\frac{b}{Z}x^{1/2}}\right]\\&-\left[\frac{bx_0}{x_0^2+bx_0+c}\right]\left[\ln\left[\frac{(r_s^{1/2}-\frac{x_0}{Z}x^{1/2})^2}{r_s+\frac{b}{Z}x^{1/2}r_s^{1/2}+\frac{c}{Z^2}x}\right]+\frac{2(b+2x_0)}{Q}\tan^{-1}\left[\frac{\frac{Q}{Z}x^{1/2}}{2r_s^{1/2}+\frac{b}{Z}x^{1/2}}\right]\right]\Bigg\}\\&+\frac{3}{5}\left[\frac{9\pi}{4}\right]^{2/3}\frac{x}{r_s^2}-\frac{3}{2\pi}\left[\frac{9\pi}{4}\right]^{1/3}\frac{Z^2}{r_s}\ \text{Ry}\ ,\end{aligned} \tag{A7}$$

which reduces to (12) for $Z \to 1$.

Similarly, the two-component analog is easily proved to be

$$\frac{E}{N} = \frac{f(Z_1^2 r_s; Z_2^2 r_s)}{r_s^2} , \tag{A8}$$

which is another exact scaling property of the two-component system.

APPENDIX B

We give here exact scaling relations for the static partial structure factors of a two-component system of particles with arbitrary masses and charges at zero temperature, and described by a Coulomb Hamiltonian with arbitrary coupling constants. We begin by assuming that the Hamiltonian contains a real parameter τ and then differentiate the Schrödinger equation for the ground state with respect to τ, which gives

$$\frac{\partial \hat{H}}{\partial \tau}|\Psi_0\rangle + \hat{H}\frac{\partial|\Psi_0\rangle}{\partial \tau} = \frac{\partial E_0}{\partial \tau}|\Psi_0\rangle + E_0\frac{\partial|\Psi_0\rangle}{\partial \tau} \tag{B1}$$

or

$$\frac{\partial|\Psi_0\rangle}{\partial \tau} = \lim_{\epsilon \to 0}(\hat{H} - E_0\hat{1} + \epsilon\hat{1})^{-1}\left[\frac{\partial E_0}{\partial \tau}\hat{1} - \frac{\partial \hat{H}}{\partial \tau}\right]|\Psi_0\rangle , \tag{B2}$$

where ϵ is a real parameter, introduced here to remove the formal singularity of $(\hat{H} - E_0\hat{1})^{-1}$ when this acts on $|\Psi_0\rangle$. This assumes no symmetry breaking or additional spurious singularities. Applying (B2) to a partial structure factor

$$S_{ab}(\mathbf{q}) = \frac{1}{\sqrt{N_a N_b}}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\langle \Psi_0|e^{i\mathbf{q}\cdot\mathbf{r}_i}e^{-i\mathbf{q}\cdot\mathbf{r}_j}|\Psi_0\rangle , \tag{B3}$$

with $a,b = \{1,2\}$, and after rescaling according to

$$\begin{aligned} \mathbf{q} &= \bar{\mathbf{q}}/r_s a , \\ \mathbf{r} &= \bar{\mathbf{r}} r_s a , \end{aligned} \tag{B4}$$

we obtain

$$\frac{\partial S_{ab}(\mathbf{q})}{\partial \tau} = \lim_{\epsilon \to 0}\frac{1}{\sqrt{N_a N_b}}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\left[\left\langle \Psi_0 \middle| \left[\frac{\partial E_0}{\partial \tau}\hat{1} - \frac{\partial \hat{H}}{\partial \tau}\right](\hat{H} - E_0\hat{1} + \epsilon\hat{1})^{-1}e^{i\bar{\mathbf{q}}\cdot\bar{\mathbf{r}}_i}e^{-i\bar{\mathbf{q}}\cdot\bar{\mathbf{r}}_j}\middle| \Psi_0\right\rangle + \left\langle \Psi_0 \middle| e^{i\bar{\mathbf{q}}\cdot\bar{\mathbf{r}}_i}e^{-i\bar{\mathbf{q}}\cdot\bar{\mathbf{r}}_j}(\hat{H} - E_0\hat{1} + \epsilon\hat{1})^{-1}\left[\frac{\partial E_0}{\partial \tau}\hat{1} - \frac{\partial \hat{H}}{\partial \tau}\right]\middle| \Psi_0\right\rangle\right] . \tag{B5}$$

Now from a general Hamiltonian of the form

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \lambda_1\hat{U}_{11} + \lambda_2\hat{U}_{22} + \lambda\hat{U}_{12} \tag{B6}$$

we obtain

$$r_s\frac{\partial \hat{H}}{\partial r_s} = -2(\hat{T}_1 + \hat{T}_2) - (\lambda_1\hat{U}_{11} + \lambda_2\hat{U}_{22} + \lambda\hat{U}_{12}) \tag{B7}$$

[after rescaling according to (B4) is performed], and also

$$\begin{aligned} &\lambda\frac{\partial \hat{H}}{\partial \lambda} = \lambda\hat{U}_{12} , \\ &\lambda_i\frac{\partial \hat{H}}{\partial \lambda_i} = \lambda_i\hat{U}_{ii} , \\ &\text{and} \\ &m_i\frac{\partial \hat{H}}{\partial m_i} = -\hat{T}_i , \end{aligned} \tag{B8}$$

with $i = 1,2$. The following combinations now result, namely

$$\begin{aligned} &r_s\frac{\partial \hat{H}}{\partial r_s} - m_1\frac{\partial \hat{H}}{\partial m_1} - m_2\frac{\partial \hat{H}}{\partial m_2} = -\hat{H} \\ &\text{and} \\ &r_s\frac{\partial \hat{H}}{\partial r_s} - \lambda_1\frac{\partial \hat{H}}{\partial \lambda_1} - \lambda_2\frac{\partial \hat{H}}{\partial \lambda_2} - \lambda\frac{\partial \hat{H}}{\partial \lambda} = -2\hat{H} . \end{aligned} \tag{B9}$$

But because the HFT with respect to any parameter,[11] in particular τ, gives

$$\left\langle \Psi_0 \left| \frac{\partial \hat{H}}{\partial \tau} \right| \Psi_0 \right\rangle = \frac{\partial E_0}{\partial \tau} \tag{B10}$$

we obtain, by taking the expectation values of (B9),

$$r_s \frac{\partial E_0}{\partial r_s} - m_1 \frac{\partial E_0}{\partial m_1} - m_2 \frac{\partial E_0}{\partial m_2} = -E_0$$

and

$$r_s \frac{\partial E_0}{\partial r_s} - \lambda_1 \frac{\partial E_0}{\partial \lambda_1} - \lambda_2 \frac{\partial E_0}{\partial \lambda_2} - \lambda \frac{\partial E_0}{\partial \lambda} = -2E_0 \ . \tag{B11}$$

The combination of (B9) and (B11) with (B5) gives

$$\begin{aligned} r_s \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial r_s} - m_1 \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial m_1} - m_2 \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial m_2} &= \lim_{\epsilon \to 0} \frac{1}{\sqrt{N_a N_b}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} [\langle \Psi_0 | (-E_0 \hat{1} + \hat{H})(\hat{H} - E_0 \hat{1} + \epsilon \hat{1})^{-1} e^{\bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_i} e^{-i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_j} | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | e^{i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_i} e^{-i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_j} (\hat{H} - E_0 \hat{1} + \epsilon \hat{1})^{-1} (-E_0 \hat{1} + \hat{H}) | \Psi_0 \rangle] = 0 \end{aligned} \tag{B12}$$

and also

$$\begin{aligned} r_s \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial r_s} - \lambda_1 \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial \lambda_1} - \lambda_2 \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial \lambda_2} - \lambda \frac{\partial S_{ab}(\bar{\mathbf{q}})}{\partial \lambda} &= \lim_{\epsilon \to 0} \frac{1}{\sqrt{N_a N_b}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} [\langle \Psi_0 | (-2E_0 \hat{1} + 2\hat{H})(\hat{H} - E_0 \hat{1} + \epsilon \hat{1})^{-1} e^{i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_i} e^{-i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_j} | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | e^{i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_i} e^{-i \bar{\mathbf{q}} \cdot \bar{\mathbf{r}}_j} (\hat{H} - E_0 \hat{1} + \epsilon \hat{1})^{-1} (-2E_0 \hat{1} + 2\hat{H}) | \Psi_0 \rangle] = 0 \ . \end{aligned} \tag{B13}$$

These are exact partial differential equations for any ground-state partial structure factor, and have the general solutions

$$S_{ab}(\bar{\mathbf{q}}) = f(m_1 r_s; m_2 r_s) \ , \tag{B14}$$

and

$$S_{ab}(\bar{\mathbf{q}}) = g(\lambda_1 r_s; \lambda_2 r_s; \lambda r_s) \ . \tag{B15}$$

These general scaling properties together with the virial theorem can be shown to be completely consistent with all scaling relations for the thermodynamic functions found in the text. For example, a two-component Coulomb system of particles of charges Z_1 and Z_2 is described by (B6) with $\lambda_1 = Z_1^2$, $\lambda_2 = Z_2^2$, $\lambda = Z_1 Z_2$. In this case (B15) gives

$$S_{ab}(\bar{\mathbf{q}}) = f(Z_1^2 r_s; Z_2^2 r_s) \ . \tag{B16}$$

In addition, the total potential energy of this system is

$$\begin{aligned} \langle U \rangle &= \frac{N}{2} \sum_{\mathbf{q} \neq 0} \frac{4\pi e^2}{V q^2} \{ Z_1^2 [S_{11}(\mathbf{q}) - 1] + Z_2^2 [S_{22}(\mathbf{q}) - 1] + 2 Z_1 Z_2 S_{12}(\mathbf{q}) \} \\ &= N \frac{2}{\pi} \int_0^\infty d\bar{q} \frac{Z_1^2 r_s [S_{11}(\bar{\mathbf{q}}) - 1] + Z_2^2 r_s [S_{22}(\bar{\mathbf{q}}) - 1] + 2 (Z_1^2 r_s)^{1/2} (Z_2^2 r_s)^{1/2} S_{12}(\bar{\mathbf{q}})}{r_s^2} \ \mathrm{Ry} \ , \end{aligned} \tag{B17}$$

so that $\langle U \rangle / N$ is of the form $f(Z_1^2 r_s; Z_2^2 r_s) / r_s^2$ because of (B16). In addition, by integrating the exact relations (48) we obtain the result that the scaling form (B16) is consistent with (A8). Similarly, by using a system with $\lambda_1 = \lambda_2 = \lambda = 1$ and (B14), a similar integration of the total potential energy gives the consistency between (B14) and (9).

The corresponding results for the structure factor of the one-component system are of course

$$\begin{aligned} & S(\bar{\mathbf{q}}) = f(m r_s) \ , \\ & S(\bar{\mathbf{q}}) = g(\lambda r_s) = h(Z^2 r_s) \ , \end{aligned} \tag{B18}$$

and they are also consistent with (11) and (A6).

It can be easily seen that all the scaling relations remain true in the same form for the corresponding pair distribution functions

$$g_{ab}(r)=1+\left(\frac{V}{N_a}\frac{V}{N_b}\right)^{1/2}\int\frac{q^2dq}{2\pi^2}\frac{\sin(qr)}{qr}[S_{ab}(q)-\delta_{ab}]$$

as well, after the rescaling (B4) is carried out.

These results can be generalized to finite temperatures by explicitly using the rescaled form of the density operator. The general results for any temperature are

$$S_{ab}(\bar{q})=f(m_1r_s,m_2r_s,Tr_s) \tag{B19}$$

and

$$S_{ab}(\bar{q})=g(Z_1^2r_s,Z_2^2r_s,Tr_s^2) \tag{B20}$$

and will be published elsewhere.

APPENDIX C

The Geldart-Vosko modification of the Hubbard form for the dielectric function[36] corresponds to the choice of local field

$$G(q)=\frac{q^2}{2(q^2+2gq_F^2)}$$

with

$$g=\frac{1}{1+\gamma r_s}\ ,$$

where

$$\gamma=0.031\frac{\pi}{2}\left(\frac{4}{9\pi}\right)^{1/3}\ .$$

In this model and from Eq. (30) we find with $y=q/2q_F$,

$$\Delta=\frac{4q_Fa}{\pi}\int_0^{\infty}dy\,S^{\text{PY}}(2q_Fy)\left(\frac{1}{\epsilon(y)}-1\right)\text{Ry}\ ,$$

with

$$\epsilon(y)=1+\frac{\dfrac{1}{\pi q_Fy^2}f(y)}{1-\dfrac{f(y)}{\pi q_F(2y^2+g)}}\ .$$

Now Ichimaru and Utsumi give $G(q)$ to be[37]

$$\begin{aligned}G(q)=&A\left(\frac{q}{q_F}\right)^4+B\left(\frac{q}{q_F}\right)^2+C\\&+\left[A\left(\frac{q}{q_F}\right)^4+(B+\tfrac{8}{3}A)\left(\frac{q}{q_F}\right)^2-C\right]\\&\times\left(\frac{4q_F^2-q^2}{4q_Fq}\right)\ln\left|\frac{2q_F+q}{2q_F-q}\right|\ ,\end{aligned}\tag{C1}$$

where the parameters A,B,C are given by

$$A=0.029\ ,$$

$$B=\tfrac{9}{16}\gamma_0-\tfrac{3}{64}[1-g(0)]-\tfrac{16}{15}A\ ,$$

and

$$C=-\frac{3}{4}\gamma_0+\tfrac{9}{16}[1-g(0)]-\tfrac{16}{5}A\ .$$

Here $g(0)$ is approximately given by

$$g(0)=\tfrac{1}{8}\left(\frac{z}{I_1(z)}\right)^2\ ,$$

where

$$z=4\left(\frac{4}{9\pi}\right)^{1/6}\left(\frac{r_s}{\pi}\right)^{1/2}\ ,$$

and $I_1(z)$ is the modified Bessel function of the first kind and of the first order; γ_0 is defined by

$$\lim_{q\to0}G(q)=\gamma_0\frac{q^2}{q_F^2}\ ,$$

and is determined by the compressibility sum rule

$$\lim_{q\to0}\chi_{\text{scr}}(q)=-n^2K$$

[where K is the ground-state compressibility

$$K=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T=0}$$

of the electron gas, and $\chi_{\text{scr}}(q)$ is determined by combination of (26) and (27)]. This leads to

$$\frac{K_0}{K}=1-\frac{4}{\pi q_Fa_0}\gamma_0(r_s)\ ,$$

where K_0 is the noninteracting value $K_0=3/2n\varepsilon_F$. We have determined γ_0 using the VWN expression [Eq. (12) with $x=1$]. The final result is

$$\gamma_0(r_s)=\tfrac{1}{4}-\frac{\pi}{48}\left(\frac{4}{9\pi}\right)^{1/3}\frac{\{r_s^{5/2}[b_0b_1R-b_0r_s^{1/2}(1+b_1r_s^{1/2})S]-4b_0r_s^2(1+b_1r_s^{1/2})R\}}{R^2}\ ,$$

where

$$R=r_s+b_1r_s^{3/2}+b_2r_s^2+b_3r_s^{5/2}$$

and

$$S=2+3b_1r_s^{1/2}+4b_2r_s+5b_3r_s^{3/2}$$

and the constants are given by $b_0=0.062\,181\,4$, $b_1=9.813\,79$, $b_2=2.822\,24$, and $b_3=0.736\,411$. In terms of this form for $G(q)$ the final result for Δ can be found from (30).

APPENDIX D

In order to obtain a better physical understanding of the calculated values of Δ with the use of $S_{pp}^{\text{PY}}(q)$, and their relation to the proton-proton correlation, we have also determined Δ for various well-known closed forms of S_{pp}, namely for totally uncorrelated protons [$S_{pp}(q)=1$, in which case $E_M=0$] and for Hartree-Fock (HF) protons ($S_{pp}(q)=\frac{3}{4}q/q_F-\frac{1}{16}q^3/q_F^3$ for $q\leq 2q_F$, and $=1$ for $q\geq 2q_F$, in which case $E_M=-0.916/r_s$ Ry). The results, compared to those of a simple PY model [where E_M is given by (39)], show that the higher the *p-p* correlation the smaller is the value of $|\Delta|$. However, as is expected, inclusion of the proton Madelung energy E_M always lowers the total energy in the case of higher proton correlation.

For the completely uncorrelated case ($S_{pp}=1$) the results should reproduce in effect those for a single proton immersed in an interacting electron gas. The HF case shows how inclusion of exchange affects the result (lowers the energy), and the third case of classical hard-sphere correlations gives an even lower energy. In all cases we have used the Ichimaru-Utsumi local field (Appendix C).

In view of the above, the fact that $|\Delta|$ is a little underestimated by the PY model for $r_s>1.4$ implies that at these low densities the protons are a little less correlated than the classical model implies [see also Fig. 6 where the PY structure factor is compared to experimental data[34] for $S(q)$ for ^{3}He]. This in fact is completely in accordance with our cage-model correction of $S_{pp}(q)$ in the text [Eq. (41)], although the major part of the disagreement is attributed to nonlinear response as discussed in the text.

In order to introduce a control or bound on the effect of the correlations incorporated in the approximate structure factor we now invoke a variational argument that will give a rigorous *upper bound* for Δ (or for the total energy). The argument will be based on the well-known Gibbs-Bogolyubov inequality,[44] namely

$$E-E_{\text{ref}}\leq\langle\hat{U}-\hat{U}_{\text{ref}}\rangle_{\text{ref}}\ . \tag{D1}$$

The "real" system is described by the Hamiltonian (2) with $\hat{U}=\hat{U}_{ee}+\hat{U}_{pp}+\hat{U}_{ep}$, but we write its energy as in (20), namely

$$E=\langle\hat{T}_e\rangle_{\lambda=0}+\langle\hat{U}_{ee}\rangle_{\lambda=0}+\langle\hat{T}_p\rangle_{\lambda=0}+\langle\hat{U}_{pp}\rangle_{\lambda=0}+N\Delta\ , \tag{D2}$$

where Δ now represents the actual value with no approximations at all. Next, take as a reference system a quantum system with the Hamiltonian

$$\hat{H}_{\text{ref}}=\hat{T}_e+\hat{T}_p+\hat{U}_{ee}+\hat{U}_{pp}^{\text{ref}}\ , \tag{D3}$$

i.e., with the same form for the kinetic energies and *e-e* interaction and with no *e-p* coupling. Here we choose $\hat{U}_{pp}^{\text{ref}}$ to be a potential-energy operator such that the ground state $|\text{ref}\rangle$ of (D3) has the property

$$\frac{\langle\hat{U}_{pp}\rangle_{\text{ref}}}{N}=E_M\ , \tag{D4}$$

where E_M is given by Eq. (39). (Note here that $\hat{U}_{pp}$ is the Coulombic *p-p* interaction term.) In other words the interaction $\hat{U}_{pp}^{\text{ref}}$ is such that the proton-proton structure factor of this unknown quantum system is given by the PY closed form (38). In this case also note that

$$\frac{\langle\hat{U}_{\text{ep}}\rangle_{\text{ref}}}{N}=\Delta^{\text{PY}}\ , \tag{D5}$$

i.e., the Δ calculated with the classical PY structure factor. According to a theorem by Henderson,[45] $\hat{U}_{pp}^{\text{ref}}$, if it exists,[46] must be unique, but is not necessarily a hard-sphere potential, since in our case we deal with a quantum system, and we do not regard S^{PY} as a classical function.[47]

The fact that there is no *e-p* coupling in the reference system implies that in its ground state

$$\langle\hat{T}_e\rangle_{\text{ref}}+\langle\hat{U}_{ee}\rangle_{\text{ref}}$$

is the same as

$$\langle\hat{T}_e\rangle_{\lambda=0}+\langle\hat{U}_{ee}\rangle_{\lambda=0}$$

for the "real" system. Therefore we have

$$E_{\text{ref}}=\langle\hat{T}_e\rangle_{\lambda=0}+\langle\hat{U}_{ee}\rangle_{\lambda=0}+\langle\hat{T}_p\rangle_{\text{ref}}+\langle\hat{U}_{pp}^{\text{ref}}\rangle_{\text{ref}}\ . \tag{D6}$$

On the other hand we have

$$\hat{U}-\hat{U}_{\text{ref}}=\hat{U}_{pp}+\hat{U}_{ep}-\hat{U}_{pp}^{\text{ref}}\ . \tag{D7}$$

Therefore the inequality (D1), in connection with (D2), (D6), and (D7), gives

$$\langle E_p\rangle_{\lambda=0}+N\Delta-\langle\hat{T}_p\rangle_{\text{ref}}\leq\langle\hat{U}_{pp}\rangle_{\text{ref}}+\langle\hat{U}_{ep}\rangle_{\text{ref}}\ , \tag{D8}$$

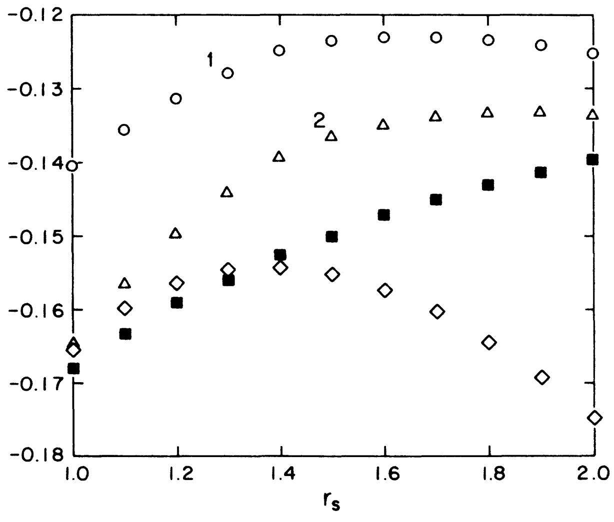

FIG. 13. Upper bounds for Δ determined by the variational principle based on a Percus-Yevick reference system [defined by (D3) and (D4) in the text]. Case 1 (circles) represents a rigorous bound (corresponding to $m\rightarrow\infty$) and case 2 (triangles) corresponds to $m=m_p$ but with the approximation (D10). The actual Monte Carlo values of Δ (diamonds), and the values of Δ calculated with the Percus-Yevick (PY) model in the text (solid squares) are also included.

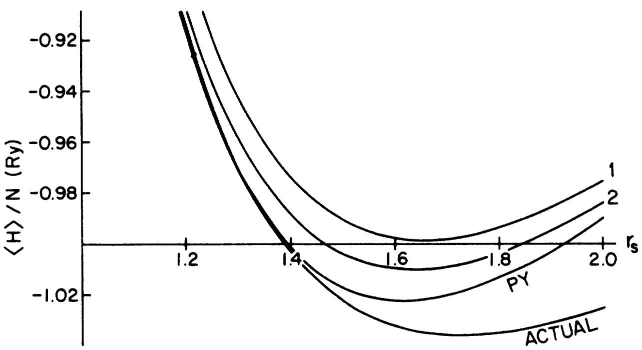

FIG. 14. The corresponding upper bounds for the total energy (20). Labels correspond to the same cases as in Fig. 13.

where we have written

$$\langle E_p \rangle_{\lambda=0} \equiv \langle \hat{T}_p \rangle_{\lambda=0} + \langle \hat{U}_{pp} \rangle_{\lambda=0} \; .$$

Note that the unknown term $\langle \hat{U}_{pp}^{\,\mathrm{ref}} \rangle_{\mathrm{ref}}$ was canceled out. Finally with the help of (D4) and D5) we obtain

$$\Delta \le E_M + \frac{\langle T_p \rangle_{\mathrm{ref}}}{N} - \frac{\langle E_p \rangle_{\lambda=0}}{N} + \Delta^{\mathrm{PY}} \; . \tag{D9}$$

This is an exact inequality relating the true Δ with Δ^{PY}. [Our treatment of the PY model was equivalent to ignoring the small unknown term $\langle T_p \rangle_{\mathrm{ref}}/N$, then using the values of η that give $E_M = \langle E_p \rangle_{\lambda=0}/N$ for each r_s, and finally taking the quality sign in (D9).]

In (D9) E_M is given by (39) and $\langle E_p \rangle_{\lambda=0}/N$ is given by the one-component result (12) with $x = 1/1836.15$. So, apart from $\langle T_p \rangle_{\mathrm{ref}}/N$ which is unknown (but small compared to the other terms), the right-hand side of (D9) is a known function of η and r_s. The form of Δ^{PY} as a function of r_s and η has to be determined by numerical integration of (30) with the PY structure factor. What remains then is to invoke the variational principle, i.e., determine, for every value of r_s, the minimum of the right-hand side of (D9) with respect to the variational parameter η. In this way we can determine a rigorous upper bound for the true Δ for every value of r_s.

By following the minimization we determine the upper bounds shown in Fig. 13. One is rigorous, corresponding to the case $m \to \infty$ (so that $\langle T_p \rangle_{\mathrm{ref}}/N$ is exactly zero), and the other uses the actual protonic mass $(m = m_p)$ and the approximation

$$\frac{\langle T_p \rangle_{\mathrm{ref}}}{N} \sim \frac{\langle T_p \rangle_{\lambda=0}}{N} \; , \tag{D10}$$

which is quite reasonable in view of the massiveness of the protons. At the same figure we also plot for comparison the actual Δ and the Δ^{PY} that we calculated in the text.

The corresponding upper bounds for the total energy (20) of the two-component system are shown in Fig. 14.

APPENDIX E

Here we discuss the $q \to 0$ behavior of $S_{pp}(q)$. We have already noted that at low proton densities, statistics are not very important, and accordingly we may take $S_{pp}(q)$ as equivalent to that of a boson problem, as discussed in the text. As a consequence $S_{pp}(q)$ vanishes linearly[23] as $q \to 0$, with a slope $\hbar/2m_p c$, where c is the speed of sound. From (41) [or more generally (36)], we find

$$\lim_{q \to 0} S_{pp}(q) = \lim_{q \to 0} S^{\mathrm{PY}}(q) = 1/\alpha$$

which is nonzero, but has a quite small value ($\sim$0.03) because of the high effective η. Note that this is about the value to which the Monte Carlo results as cited in the literature[5] seem to tend. However, we expect[6] that at a very small q the structure factor becomes linear. In the text a simple form[24] to account for this long-range behavior was given [Eq. (31)]. Here we give a dimensional argument to estimate how small q_c actually is.

We basically need to reconcile our Einstein model with the Debye model implicit in the existence of c. This requires a mass-dependent cutoff q_c (for example, in the limit $m_p \to \infty$, there is strictly zero overlap between the oscillators, which implies that no collective effect can be established, which in turn implies that $q_c \to 0$). A rough estimate of q_c can be obtained from the following argument

$$\frac{2r_s a}{\dfrac{2\pi}{q_c}} \le \frac{(\langle u^2 \rangle)^{1/2}}{\left[\dfrac{V}{N}\right]^{1/3}}$$

that gives an upper bound for q_c, namely

$$q_c \le \frac{1}{r_s^{1/4}} \left[\frac{m_e}{m_p}\right]^{1/4} \frac{1}{a} \equiv \bar{q}_c \; . \tag{E1}$$

Now even for q_c as large as the upper bound $\bar{q}_c$, the resulting $S_{pp}(q)$ is identical to the one used in the text, apart from very near $q=0$, where it goes to zero linearly with the right slope. We also find from (30) that even for this case the effects on Δ are small ($<10\%$).

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