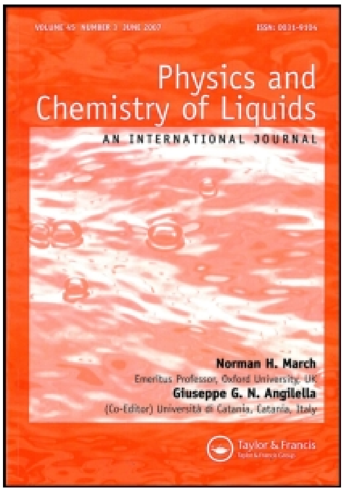

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SINGLE-PARTICLE SCATTERING APPROXIMATION FOR THE PAIR FUNCTION OF AN ELECTRON LIQUID

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The static pair correlation function of the three-dimensional homogeneous electron gas at given temperature and density is estimated by the scattering of non-interacting particles in an effective potential. Within a generalized Thomas–Fermi approximation the resulting self-consistency conditions can be reduced to a simple linear differential equation. The influence of temperature and interaction on the short-range correlations is investigated extensively. The comparison with ground-state Monte-Carlo calculations shows an excellent conformity at metallic densities.

KEY WORDS: Jellium, nonzero temperature, pair function, effective interaction

1 INTRODUCTION

The pair correlation function $g(r)$ of the homogeneous jellium system has been studied intensively since the early beginning of the electron gas theory. It is defined as the probability of finding two electrons separated by a given distance r, and thus reflects the structural complexity of the many-particle system. After four decades of development in this field various approximations are available that satisfactorily describe more or less properties of this function at zero temperature[1]:

Approaches using the dielectric formalism are based on a truncated energy and momentum excitation balance. Well known representatives of this class are the *Random-Phase-Approximation* (RPA)[2], the *Singwi-Tosi-Land-Sjölander theory* (STLS)[3], and the diagrammatic analysis by Yasuhara[4,5]. Most of these models, however, (with the exception of Yasuhara's theory) significantly overestimate the short-range correlations at metallic densities. Consequently, other methods have been introduced to overcome this problem, as, for example, the very successful *Fermion Hypernetted Chain theory* (FHNC)[6] or the *Pseudoclassical Approach*[7].

Although one can say that the static ground-state correlations of the completely degenerate Fermion system are hence well understood, the situation is getting much worse when going to nonzero temperature: Only a few generalizations of well established approximations are yet available for this problem[8–10].

Additionally, an interesting new effect has been discovered recently by Schweng *et al.*[10]: Studying the temperature dependence of the short-range correlations in various approximations they found that $g(0)$ *does not* increase monotonically with increasing temperature, as one would expect. Instead, a decrease is found for small temperatures. The physical mechanisms behind this are temperature-dependent screening effects, as could be shown clearly within a single-particle model of the real-space scattering balance[10].

This success of a relatively simple approach gives strong evidence that it might pay to take a closer look at approximations, which describe the short-range correlations as a tunneling probability of quasi-free electrons in an effective, self-consistently determined potential. The main objective of this work will be the development and analysis of such a model.

This paper is organized as follows: In Section 2 the basic assumptions of a *Single-Particle Scattering Approximation* (to be referred to as "SPSA" throughout this paper) for the pair correlation function will be discussed. Writing down the self-consistency equations several limiting cases can already be evaluated.

In Section 3 it is shown that an additional linearization step transforms the self-consistency problem into an almost analytically solvable equation. This makes it possible to explicitly analyse the competing physical effects that are responsible for the temperature dependence of $g(r)$.

Various numerical results of this approximation will be presented in Section 4, and a brief discussion in Section 5 ends this paper.

2 BASIC ASSUMPTIONS

Coarsely spoken, the basic principle of a *Single-Particle Scattering Approximation* (SPSA) for the static pair correlations is the following: Within the interacting electron gas one electron at the (arbitrarily chosen) origin is considered to be the source of an effective single-particle potential, in which the (approximative mutually non-interacting) collective is "moving". It is then reasonable to assume that the effective interaction is determined by the radial charge distribution around the origin, which itself is given by $1 - g(r)$. This immediately leads to Poisson's equation

$$\Delta U(x) = -8\pi\alpha r_s \left\{ \delta(\mathbf{x}) - \frac{1}{3\pi^2}\,[1 - g(x)] \right\}. \tag{1}$$

In Eq. (1) the following units have been used, as will be throughout the rest of this paper: Distances are measured in the inverse Fermi momentum k_F^{-1}, while energies are given in Fermi energies E_F. The usual density parameter r_s is connected with the average density n_0 by the relation $r_s = a_B^{-1}(\frac{4}{3}\pi n_0)^{-1/3}$; a_B denotes the Bohr radius. Furthermore, α is an abbreviation for $(4/9\pi)^{1/3}$.

The term proportional to $\delta(\mathbf{x})$ is the point-charge density of the electron at the origin and causes $U(x)$ to behave like a bare Coulomb potential for $x \to 0$, while the

"1" in the square brackets takes into account the uniform, positive background of the jellium model.

Now, there are several possibilities to close the approximation, i.e. to write down the pair correlation function $g(x)$ as a functional of the effective interaction $U(x)$. For example, a very interesting way has been proposed by Dawson and March, who expressed the pair function in terms of the p-component of the electron density matrix[11–13].

Within the present work, however, another, perhaps more obvious method will be used: The electron that is "carrying" the effective single-particle potential can be interpreted as an "impurity", embedded in a free electron liquid. One then can take advantage from the analysis by March and Murray[14], and write down the expressions:

$$\left\{\frac{\partial^2}{\partial x^2} + k^2 - \frac{1}{2}\,U(x) - \frac{l(l+1)}{x^2}\right\}u_{kl}(x) = 0 \tag{2}$$

$$n_l(x|U) = \frac{3}{2}\int_0^\infty dk\; n_k^0(\theta,\mu)\xi_l(k)\left(\frac{u_{kl}(x)}{x}\right)^2 \tag{3}$$

$$\xi_l(k)^{-1} \equiv \lim_{z\to\infty}\frac{1}{z}\int_0^z dx[u_{kl}(x)]^2 \tag{4}$$

$$n(x|U) = \sum_{l=0}^{\infty}(2l+1)n_l(x|U). \tag{5}$$

Eq. (2) just is the radial part of Schrödinger's equation; the factor "$\frac{1}{2}$" beside the potential $U(x)$ is caused by the fact that the "impurity" has electron mass too. Eq. (3) defines the radial density components n_l (in units of n_0); $n_k^0(\theta,\mu)$ denotes the free Fermi distribution at reduced temperature $\theta \equiv k_BT/E_F$ and (free) chemical potential μ. The quantity $\xi_l(k)$ as defined by Eq. (4) takes into account the correct normalization of the wave function. Finally, summing up the partial density components one obtains the total density of the free electron liquid in the presence of a single-particle potential $U(x)$.

The final step, however, is the most critical one, namely, the connection between $n(x|U)$ from Eq. (5) and the (approximated) pair function. Writing down the spin-parallel and -antiparallel pair functions as a decomposition into their free counterparts and an unknown functional of the density

$$g_{\uparrow\uparrow}(x) \simeq g^0_{\uparrow\uparrow}(x)F_{\uparrow\uparrow}[n-1;x] \tag{6a}$$

$$g_{\uparrow\downarrow}(x) \simeq g^0_{\uparrow\downarrow}(x)F_{\uparrow\downarrow}[n-1;x] \tag{6b}$$

it is clear that $F_{\uparrow\uparrow}[0;x] = F_{\downarrow\uparrow}[0;x] = 1$ is necessary to correctly obtain the high-density limit. Since $g_{\uparrow\uparrow}(x)$ does not contribute to the short-range correlations, as a first attempt $F_{\uparrow\uparrow}$ will be set to "1". Further simplification can be achieved when substituting the remaining functional by a *function* of $n(x) - 1$, and then expanding this function up to the first order. This finally leads to

$$g(x|U) \simeq g^0(x) + \tfrac{1}{2}[n(x|U) - 1], \tag{7}$$

where the remaining expansion coefficient has been set to "1", in order to obtain

$$g(0|U) = \tfrac{1}{2}n(0|U) \tag{8}$$

in accordance with Eq. (25) of Ref. [10]. $g^0(x)$ denotes the free spin-averaged pair function. (The temperature dependence of $g^0(x)$ will be omitted for brevity).

Although the steps leading to Eq. (7) somehow might have the flavour of a magician's trick, there are justifying arguments for them when looking at the system at a certain "mesoscopic" level: The ansatz Eq. (6) then is a factorization of expectation values into a (free) statistical part and a factor that accounts for the interaction effects. Linearizing the functional corresponds to a weak-coupling expansion, and substituting the functional by a function means neglecting some delocalisation effects (the functional's kernel is set to a delta-function). The reader, however, should be aware of the fact that the ansatz Eq. (7) indeed might be the *simplest*, but most probably not the *optimal* ansatz for a SPSA.

Nevertheless, it is the intention of this work to investigate the simplest possible case, which, as we shall see, already leads to remarkable results.

Now, combining Eqs. (2)–(5) with Eq. (7), in principle, reduces the problem to a numerical one. Three important results, however, can be derived immediately:

i) One of the most striking features of a SPSA obeying Eq. (8) perhaps is the fact that

$$g(r) > 0 \tag{9}$$

exactly holds.

ii) Looking at the $x \to 0$ behaviour of Eqs. (2)–(5) it is easily seen that

$$n'(0|U) = \alpha r_s n(0|U), \tag{10}$$

as long as $U(x \to 0)$ behaves like a bare Coulomb potential. Inserting this into Eq. (7) proves that Kimball's relation[15]

$$g'(0) = \alpha r_s g(0) \tag{11}$$

is exactly fulfilled by the present approximation.

iii) Evaluating Eq. (8) using Born's first-order approximation yields for $\theta = 0$:

$$g(0|U) = \frac{1}{2} - \frac{3}{4}\int_0^\infty dx\ U(x) j_1(2x) + \mathcal{O}(U^2), \tag{12}$$

with $j_1(x)$ being the first-order spherical Bessel function. Inserting the free pair function into the right-hand side of Eq. (1), and combining its solution with Eq. (12) leads to

$$g(0) \simeq \tfrac{1}{2} - 0.4347 \cdot r_s + \mathcal{O}(r_s^2). \tag{13}$$

Comparing Eq. (13) with the exact high-density expansion obtained by Kimball[16]

$$g(0) \simeq \tfrac{1}{2} - 0.3658 \cdot r_s + \mathcal{O}(r_s^2 \cdot \ln r_s), \tag{14}$$

a good conformity is found.

3 GENERALIZED THOMAS–FERMI APPROXIMATION

In the previous section the basic assumptions leading to a typical *Single-Particle Scattering Approximation* have been pointed out. The remaining numerical problem, however, is somehow unwieldy, and it would be advantageous for a clear physical analysis if one could separate the calculation of $U(x)$ from the evaluation of Eqs. (2)–(5). This can be achieved by using a generalized Thomas–Fermi approximation for the density equilibrium:

Assuming a slowly varying potential $U(x)$, Eqs. (2)–(5) can be reduced to

$$n(x\,|\,U) \simeq n_{TF}(x\,|\,U) = 3\int_0^\infty dk\; k^2 n_k^0\left(\theta,\, \mu - \frac{1}{2}\, U(x)\right). \tag{15}$$

Furthermore, expanding Eq. (15) up to first order with respect to $U(x)$ yields

$$n_{TF}(x\,|\,U) \simeq 1 - \frac{1}{\theta}\, S_{q=0}^0(\theta)\, \frac{1}{2}\, U(x), \tag{16}$$

where $S_{q=0}^0(\theta)$ denotes the static structure factor of the free system at momentum $q = 0$ and temperature θ, and is given by

$$S_{q=0}^0(\theta) = 3\theta \int_0^\infty dk\; k^2 \frac{\partial}{\partial \mu}\, n_k^0(\theta, \mu). \tag{17}$$

Introducing the abbreviations

$$\lambda(\theta)^2 \equiv \frac{2}{3\pi}\, \alpha r_s\, \frac{1}{\theta}\, S_{q=0}^0(\theta) \qquad \text{and} \qquad h(x) \equiv \frac{4}{3\pi} x[1 - g^0(x)], \tag{18}$$

one finally obtains

$$\left[\frac{\partial^2}{\partial x^2} - \lambda(\theta)^2\right] f(x) = h(x) \tag{19}$$

for the *screening factor* $f(x)$ that is defined as $U(x)$ divided by a bare Coulomb potential. Obviously, Eq. (19) has to be completed by the boundary conditions

$$f(0) = 1 \qquad \text{and} \qquad f(x \to \infty) \to 0, \tag{20}$$

leading to the solution

$$f(x) = e^{-\lambda(\theta)x} + \int_{-\infty}^{\infty} ds\, G(x - s)h(s), \tag{21}$$

where

$$G(x) = -\frac{1}{2\lambda(\theta)} e^{-\lambda(\theta)|x|} \tag{22}$$

is the Green's function of Eq. (19).

The physical interpretation of Eq. (21) now is obvious: The approximated screening factor consists of an exponentially decaying term that is a pendant to the perfect-screening behaviour of the RPA, and a second term that decays obeying a power-law. It is the latter part that is producing overscreening effects, i.e. $f(x)$ becomes negative for large x. It is especially noteworthy that for zero temperature

$$\lambda(0)^2 = \tfrac{1}{4}q_{TF}^2 \tag{23}$$

holds (q_{TF} is the Thomas–Fermi screening vector). Thus, the present result differs in two important points from the usual Thomas–Fermi approach: (i) One factor "$\frac{1}{2}$" in Eq. (23) stems from the reduced electron mass (confer Eq. (2)). (ii) The second factor "$\frac{1}{2}$" in Eq. (23) and the additional integral term in the solution Eq. (21) are consequences of the "functional"-ansatz Eq. (7).

Finally, the qualitative temperature dependence of $f(x)$ can be seen directly from Eq. (21): $\lambda(\theta)$ varies very slowly with respect to θ as long as $\theta \lesssim 1$, and for $\theta \gg 1$ it vanishes like $1/\theta$ (confer Eq. (18)). Within the main region of interest ($\theta \leq 1$) one therefore can set $\lambda(\theta) \approx \lambda(0)$ and just take into account the temperature dependence of the inhomogeneity $h(x)$. With increasing θ the free pair function tends to its classical counterpart (which is simply equal to one) and consequently $h(x)$ will vanish. Thus, the range of the potential barrier $U(x)$ is increased, which *lowers* the tunneling probability of the electrons, and decreases $g(0)$. On the other hand, however, the mean kinetic energy of the gas is also increased with increasing θ, which again *rises* the tunneling probability (confer Eq. (3)).

Now, it is not *a priori* clear, which one of these two competing effects is going to win for a given temperature and coupling strength. The analysis of Schweng *et al.*[10] has shown that the negative slope in the temperature behaviour of $g(0)$ is present for small θ, when neglecting second-order terms with respesct to r_s. It is interesting to learn from Eq. (21) that higher-order interaction terms indeed can cancel this effect, since the exponential term in Eq. (21) provides an upper boundary for $f(x)$. Consequently, the "thickness" of the potential barrier cannot be increased too much with increasing θ, when r_s (and λ with it) tends to infinity.

4 NUMERICAL ANALYSIS

Combining Eqs. (18), (21) and (22) the screening factor $f(x)$ can easily be obtained. With the resulting potential $U(x)$ one has to solve Eqs. (2)–(5) and (7). From the computational point of view this is a much more complicated task, since it involves the numerical solution of Schrödinger's equation (Eq. (2)) for an (almost) arbitrary $U(x)$. Thereby one has to overcome the problem of round-off errors that are mixing parts of the divergent solution of Eq. (2) to the desired non-divergent one. These numerical instabilities cause standard one-step integration methods to fail. An *implicit* Runge–Kutta algorithm of Gaussian type (*order* $m = 2$, *consistency order* $p = 4$)[17] has turned out to be sufficiently stable as well as fast. The remaining integral and sum can be easily carried out, although they are rather time-consuming. In this context it is especially noteworthy that for the calculation of $g(0)$ only the $l = 0$ term of the sum in Eq. (5) is necessary, since $n_l(x)$ is proportional to x^{2l} as $x \to 0$.

In Figure 1 the r_s-dependence of $g(0)$ at zero temperature is compared with the results of Yasuhara's theory[5]. A very good conformity is found, even in the low-density regime. This is especially remarkable, since the derivation of Eq. (19) involved an additional small-r_s expansion step.

In Figure 2 the deviation of $g(0, \theta)$ from the interaction-free value "$\frac{1}{2}$"

$$\Delta g(0, \theta) \equiv [g^0(0, \theta) - g(0, \theta)]/r_s, \tag{24}$$

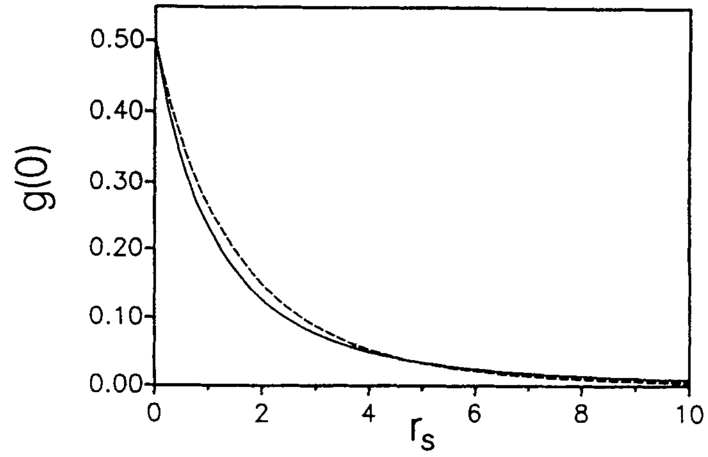

Figure 1 The pair correlation function $g(r = 0)$ at zero temperature versus r_s from the present calculations (solid line) and the Yasuhara theory[5] (dashed line).

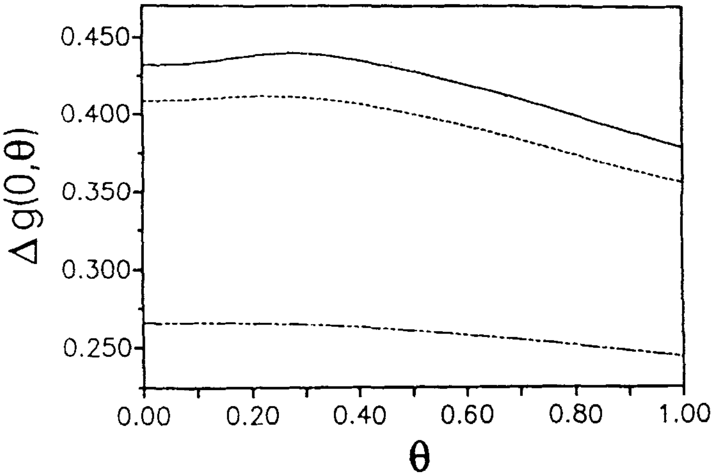

Figure 2 Correction term to the result of the free pair correlation function at zero particle separation versus temperature θ (confer Eq. (24)). Solid line: $r_s = 0.01$; dashed line: $r_s = 0.1$; dash-dotted line: $r_s = 1$.

divided by r_s is plotted versus temperature for various r_s. The curve corresponding to $r_s = 0.01$ already is almost identical to the result in Figure 5 of Ref. [10], where an explicit first-order expansion has been carried out. Furthermore, it is seen that increasing r_s indeed reduces the "negative-slope effect", until at $r_s = 1$ the resulting $g(0)$ within the numerical accuracy is monotonically increasing with increasing θ. For extremely high r_s-values the effect is (very weakly) appearing again, since the

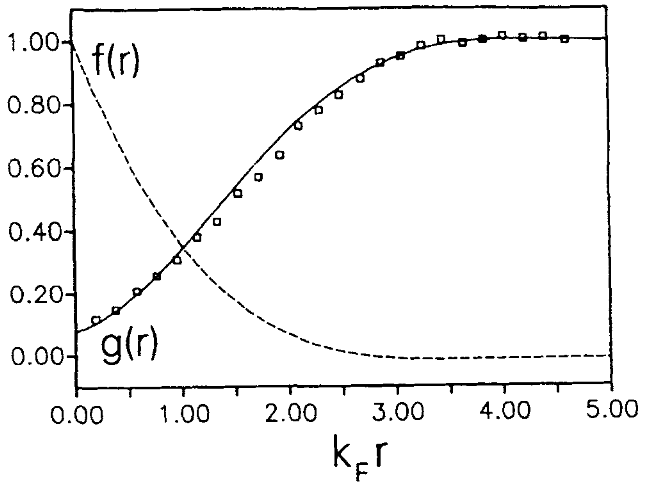

Figure 3 The pair correlation function $g(r)$ (solid line) and the screening factor $f(r)$ (dashed line) at zero temperature versus $k_F r$, calculated from the present approximation. The squares are the results of a Monte-Carlo simulation; the data have been taken from Figure 3 of Ref. [19].

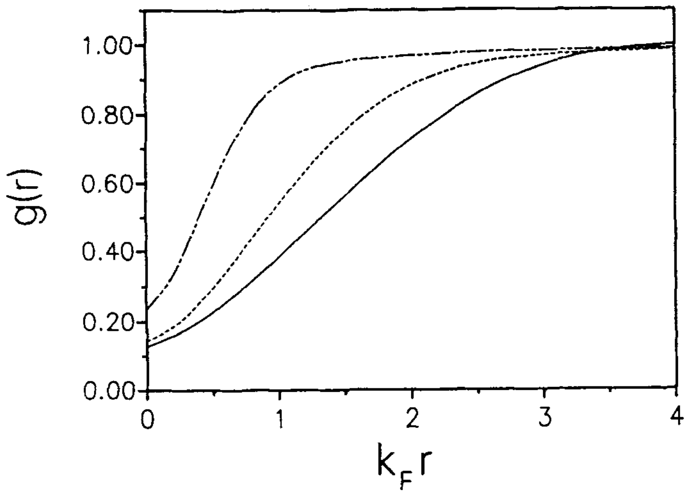

Figure 4 The pair correlation function $g(r)$ at $r_s = 2$ versus $k_F r$. The curves correspond to the temperatures $\theta = 0$ (solid line), $\theta = 1$ (dashed line), and $\theta = 5$ (dash-dotted line).

θ-dependence of λ must be taken into account in this case. It is, however, at least questionable to extend the present approximation on to that region.

The corresponding results for the complete $g(r)$ at $r_s = 3$ and $\theta = 0$ are shown in Figure 3. The conformity with a Monte-Carlo calculation[18] is excellent (the MC-values have been taken from Figure 3 of Ref. [19]). However, it should be mentioned that the situation becomes less satisfactory when going to very high values of the coupling parameter, $r_s \approx 100$: The overscreening effects in $f(x)$ are too weak to produce the significant large-x oscillations that are announcing the Wigner crystallisation[20]. Again one should bear in mind that this extreme region is beyond the scope of the present approximation.

Finally, $g(r)$ at $r_s = 2$ is plotted for various temperatures in Figure 4.

5 CONCLUSIONS

In the previous sections it has been shown that the simple *Single-Particle Scattering Approximation* presented here already provides a surprisingly realistic description of the static pair correlations at arbitrary temperature. And this even, although the full self-consistency problem has been substituted by a Thomas–Fermi like approach, which, in principle, is used here outside the region of validity for such a quasiclassical approximation. A comparison of the present results with the numerical solution of the full self-consistency equations, however, justifies this simplification, as will be published in the near future.

Despite of its undeniable success the present concept of SPSA, of course, does have its disadvantages, too: The problem with the unrealistic large-x behaviour at extremely low densities has already been discussed earlier. Closely related with this is the unpleasant fact, that the ansatz Eq. (7) does not guarantee the normalization condition

$$\int d^3x[1 - g(x)] = 3\pi^2 \tag{25}$$

(often referred to as "sequential relation") to be fulfilled exactly. (It should be noticed that the integral over $n(x) - 1$ in Eq. (7) is proportional to the total displaced charge, which itself is, within first-order perturbation theory, proportional to the interaction volume[21].) Although the deviations from the exact fulfillment of the sequential relation are neglectable for practical purposes, this fact gives strong evidence that the replacement of Eq. (7) by a more sophisticated ansatz might be rewarding.

Of course, even using an optimal functional instead of Eq. (7) the SPSA still will neglect many-particle effects. Consequently, the question is still pending, whether the complex interplay of temperature and interaction dependencies leading to $g(0, \theta)$ is modeled realistically enough by looking at a tunneling process only. It will be an important as well as extensive task to answer this question within a reliable first-principles theory, most probably an evaluation of the *ladder-diagram* sum for nonzero temperature.

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